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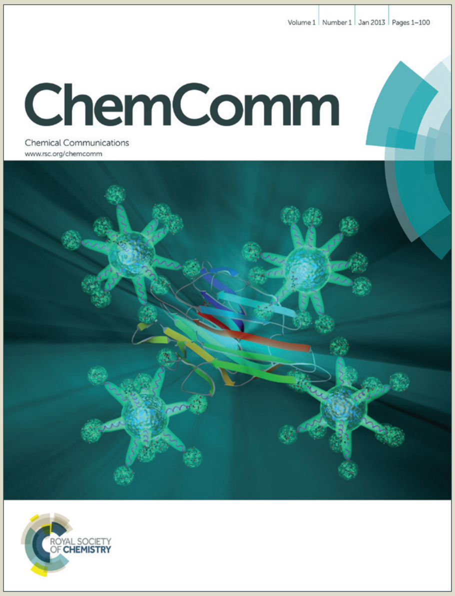
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ARTICLE TYPE

Observation of allylic rearrangement in water-rich reaction

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Allylic rearrangement or the migration of a double bond from its original position in the carbon skeleton to an adjacent site was observed when 3,4,5,6-tetrahydrophthalate was hydrolyzed in a basic solution and in the presence of Co(II) and Mn(II) under hydrothermal conditions.

Metal-ligand reactions under solvo(hydro)thermal conditions frequently produce unexpected results.[1,2] The in situ transformation of the original ligands leads to the production of ligands that are not readily accessible or at all possible if the reactions are carried out under normal conditions, and the newly formed ligands are responsible for the formation of the often interesting structures of the resulting complexes.[3-7] Albeit interesting and practically useful, except for a small number of thoroughly investigated cases, the majority of such reactions remain mechanistically unclear. As such, the "rational synthesis" of metal-ligand complexes with pre-designed structures under such conditions is an inexact science. Exploratory synthesis, with the hope of discovering new materials with useful properties, has been a common alternative.[1,2]

In this work we report a hitherto unknown example of allylic rearrangement reaction under hydrothermal conditions. More significantly, with the isolation of a complex featuring the coordination of both the original ligand and the newly formed ligand, and coupled with computational studies, the mechanism of this rearrangement reaction can be reasonably established.

The unusual allylic rearrangement under hydrothermal conditions was observed when we attempted the synthesis of Co(II)-containing coordination polymers for magnetic studies. The ligand to be used was cyclohexene-1,2-dicarboxylate (1,2-chedc, **2**), which can be generated by the basic hydrolysis of 3,4,5,6-tetrahydrophthalic anhydride (THPA, **1**). Unexpectedly, a crystalline product of the formula ${}^{2}_{\infty}[\mathrm{Co^{II}(2,3\text{-}chedc)(DABCO)_{0.5}}]$ (**1Co**), (2,3-chedc, cyclohexene-2,3-dicarboxylate; DABCO, 1,4-diazabicyclo[2.2.2]octane) was isolated from the reaction of a mixture (pH ≈ 9) containing $CoCl_2$, THPA, and DABCO under hydrothermal conditions (See Supporting Information for experimental details); the dicarboxylate ligand is 2,3-chedc rather than 1,2-chedc anticipated from the hydrolysis of THPA (Fig. 1).

The structure of **1Co** was determined crystallographically. As shown in Fig. 2a, its asymmetric unit contains one Co, one 2,3-chedc, and half a DABCO. The Co(II) ion adopts a slightly distorted square-pyramidal coordination geometry with its four basal carboxylato O atoms (Co−O 2.026(3)−2.077(3)Å) from different 2,3-chedc ligands and one N from DABCO (Co−N 2.113(3)Å). The position of the C=C bond can be unambiguously determined to be between C2 and C3 as the metric value of the C2−C3 distance of 1.314(5) Å is consistent with that of a normal C=C bond and significantly shorter than that of a typical C-C bond (C1−C2 1.507(5) Å).

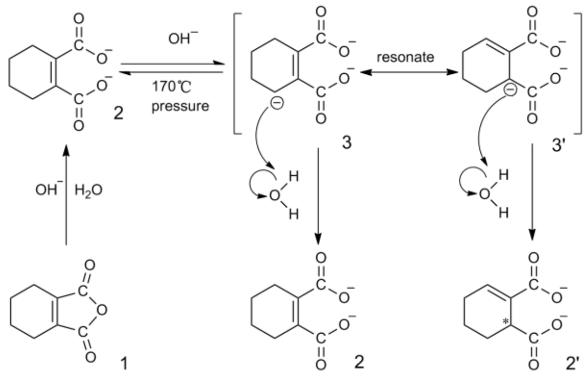

Fig. 1. S$_{E}$1 mechanism for forming 1,2-chedc (**2**) and 2,3-chedc (**2'**). * indicates the chiral carbon site in **2'**. We have isolated only the product **2'** in **1Co**, whilst both **2** and **2'** in **2 Mn**.

The most salient feature of 2,3-chedc is the existence of a chiral center (C1, Fig. 2a), leaving the adjacent carboxylate group "twisted" to the α-position of the ring structure, lowering the symmetry of the ligand to C_s, and imparting the ligand with much enhanced flexibility in metal coordination over the anticipated 1,2-chedc whose two carboxylate groups are rigidly *cis*-disposed with respect to the C=C bond. However, the crystalline solid is just a racemic conglomerate as the ligands are present as racemic pairs in the crystal structure. The overall structure can be conveniently described as the dinuclear unit of Co(II) being bridged by carboxylate groups of different 2,3-chedc ligands, resulting in a paddle-wheel-like structure which is further extended into a chain along the crystallographic *a*-axis (Fig. 2b) due to the bridging interactions between the repeating Co_2 units using the second carboxylate group of each of the four dicarboxylate ligands. The individual chains are interlinked via the coordination of Co centers with DABCO at the apical position, affording a two-dimensional (2D) grid-like sheet (Fig. S1a), which stacks along the crystallographic *b*-direction in an offset ABAB fashion to generate the lamellar structure. It is interesting to note that the two centrosymmetrically related coordination square-pyramids are not collinear but with the N1−Co1⋯Co1a angle of 163.90(9)° due to the significantly "twisted" carboxylate groups; the Co(II) ions are forced to be closer to one of the carboxylate *O* atom than to the other (Co1a···O2 2.81 Å versus Co1a···O1a 3.57 Å), as shown by the green dotted lines in Fig. S1a.

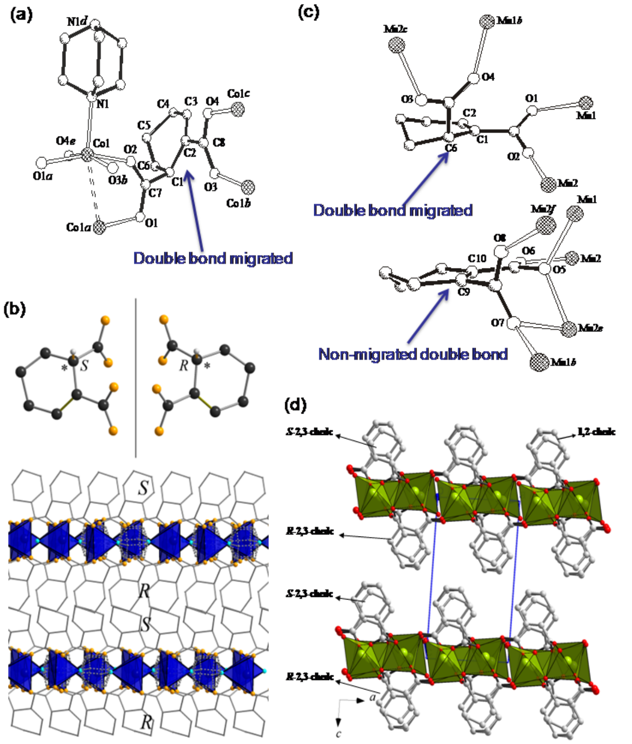

Fig. 2. The ligand conformations of **1Co** (a) and **2Mn** (c) show migrated and non-migrated double bonds; the racemic pair of 2,3-chedc and their organizations in the crystal packing of **1Co** (b) and **2Mn** (d). Symmetry codes: for **1Co**, *a*)-x+1, -y, -z; *b*) -x, -y, -z; *c*) x-1, y, z; *d*) -x+1, -y, 1-z; *e*) x+1, y, z; for **2Mn**:*b* -x+1, -y+2, -z; *c* -x+3, -y+1, -z; *e* -x+2, -y+2, -z; *f* -x+1, y, z.

Considering the reaction conditions, it is reasonable to hypothesize the formation of 2,3-chedc by S_E1 mechanism as schematically shown in Fig. 1. With the presence of DABCO as a Brønsted base, THPA undergoes hydrolysis to afford the anticipated 1,2-chedc. The CH_2 site that is α to the carboxylate groups is activated toward deprotonation, and the resulting carbanion (**3**) is in resonance with a more stable tertiary cabanion form (**3'**). Re-protonation of **3** and **3'** affords 1,2-chedc and 2,3-chedc, respectively. These different ligands can subsequently participate in metal coordination to produce the coordination polymers observed.

It is very difficult to uncover the mechanisms of complex organic reactions in hydrothermal reactions. So far only exceptional cases of such reactions have been thoroughly investigated.[5] We cannot exclude an S_E2' mechanism caused by the direct attack of electrophiles on the carbon backbone (Scheme S1) simply based on the crystal structure of **1Co**. Meanwhile, it is well-known that some transition metal catalysts (complexes containing Pt, Rh, or Ru, or metal carbonyl catalysts) can catalyze the double bond migration in two pathways (Scheme S2).[8a,13] Considering the transition metal ion (Co^{2+}) and other ligands in our system, we also cannot exclude these possibilities, and need further concrete evidence for understanding the mechanism in our system. The isolation of intermediates of the two resonance-stabilized cyclohexenedicarboxylates (**3** and **3'**) is obviously crucial.

After trying we were able to capture such intermediates in the solid structure of $^{2}_{\infty}[Mn^{II}_2(1,2\text{-chedc})(2,3\text{-chedc})(H_2O)]$ (**2Mn**). **2Mn** crystallizes in the triclinic space group *P*-1. As shown in Figure 2c, the two cyclohexene-dicarboxylates have disparate coordination modes. For non-migrated product the C=C bond locates between two carboxylates groups, so that carbon atoms connect to C=C (herein: C9 and C10) are confined in the same plane, leaving only the carboxylato-*O* atoms rotate about the C–C axes. For migrated product the chiral carbon atom (C6) forms with similar "twisted" *α*-position of the ring structure as in **1Co**. Again, the crystalline solid is just a racemic conglomerate as the ligands are present as racemic pairs in the crystal structure (Fig. 2d). Two kinds of coordination polyhedra of Mn(II) are found in the structure, one being a pseudo-octahedron and the other trigonal. The average Mn···Mn separation and Mn–O–Mn angle in the $\{Mn_4\}$ square are 3.70 Å and 114.11(7)°, respectively. The nearest Mn···Mn separations between the $\{Mn_4\}$ squares and between the chains are 4.20 and 4.92 Å, respectively. With the perpendicular fashion the two carboxylates in 1,2-chedc adopt the μ^3-η^2:η^1 mode to form the basic corner-shared $\{Mn_4\}$ square, which is further linked by quadruple *μ*-carboxylates into a 1D chain running along the *a*-axis (Fig. S1b). The individual chains are further bridged by racemic pairs of 2,3-chedc ligands in a more flexible bis(μ-η^1:η^1) mode, generating a 2D layered structure. The layers stack into a 3D crystal structure *via* van der Waals interactions with the shortest Mn···Mn separation of 12.70 Å along the crystallographic *c*-direction.

We have subsequently performed DFT calculations in seeking theoretical understanding of the experimental results, in particular the metal-dependence of the observed rearrangement.[10] Fig. 3 shows the potential energy surface and the geometries of key stationary states of the reaction of cyclohexene-1,2-dicarboxylic acid (1,2-chedcH_2, m1) with OH^- and two H_2O molecules. The first step along the reaction coordinate corresponds to the formation of an O···H hydrogen bond (m2) of 1.98Å between one O atom of the $OH^-/(H_2O)_2$ cluster and one of the H atom (H4) of the *α*–CH_2 (*sp*^{3}-hybridized C1) of 1,2-chedcH_2, accompanied by the lowering of energy of 12.7 kcal/mol. This H atom then moves closer to the OH^-, resulting in a transition state (ts2/3) with an increase of energy of 3.5 kcal/mol, followed by its complete departure from the *α*–C (C1) and transfer onto the $OH^-/(H_2O)_2$ cluster (m3) with a small lowering of energy of 0.7 kcal/mol. The charge is then redistributed to extend the conjugation over the skeleton of C3, C2, and the now *sp*^{2}–hybridized C1. In the meantime, the newly formed $(H_2O)_3$ cluster migrates from above C1 to above C3, leading to state m3' which is more stable than m3 by 3.9 kcal/mol that may be attributable to the extra hydrogen bonds formed between the water cluster and the two carboxyl groups. The process concludes by the transformation of m3' to m4 with the transition state of ts3'/4. In this step, a proton migrates from the water cluster to the *sp*^{2}–hybridized C3 atom, resulting in the chiral C (*sp*^{3}–hybridized C3) centre in the rearranged product of cyclohexene-2,3-dicarboxylic acid (2,3-chedcH$_2$). Thus, the formation of double-bond migrated product can be well explained by this OH$^-$/H$_2$O assisted S$_E$1 mechanism. Note that the energy differences of each well in this process are merely in the energy scale of hydrogen bonds[11] and thus the isolation of intermediate products becomes possible.

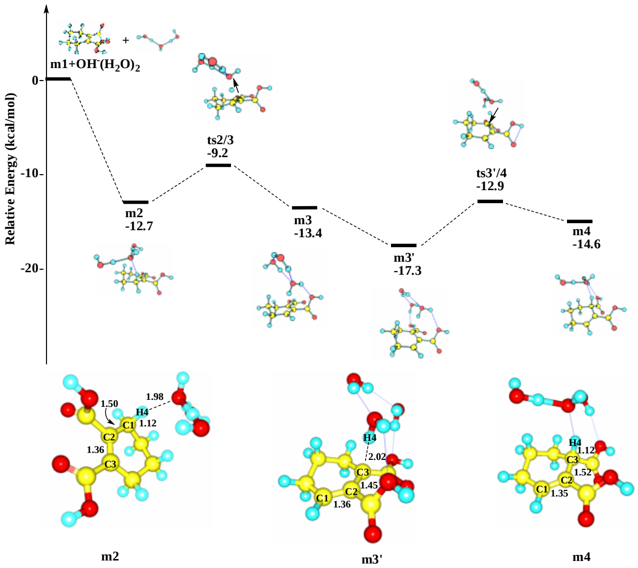

Fig. 3. Potential energy surface and structures corresponding to the stationary points in the reaction of the cyclohexene-1,2-dicarboxylic acid with OH-(H$_2$O)$_2$ (bond lengths in angstroms).

In experiments, the reactions were carried out with Mn(II) and Co(II) ions, and a preference for different double bond positions (C2-C3 and C1-C2) has been observed. To better represent the periodic molecular-metal chain products, for each metal ion, we added two metal atoms to the current model by complexing them with the -COO$^-$ groups, furnishing m3-Co and m3-Mn, respectively (Fig S2). The NBO analysis results indicate that m3-Mn has a natural charge of -0.25e on C1 and -0.26e on C3. However, in m3-Co, C1 has a charge of -0.26 e, while the charge on C3 is -0.30e, a much bigger difference. The position of the double bond depends on the nucleophile strength of the proton-accepting carbon atoms, i.e. the bigger the negative charge on a C atom, the easier the protonation at that C position. As the charges on C1 and C3 in m3-Mn are very close, the protonation has approximately equal probability at either carbon positions and thus two isomeric products are obtained. In contrast, in m3-Co, the big charge difference leads to a much favored C3 protonation and only one product is detected. As such, the charge difference caused by Co(II) and Mn(II) on the C1 and C3 is likely to be the reason for observing different product preference. We would like to point out that the product preference might also be tuned by other metals and even substitution groups (Fig. S2).

To summarise, hydrolysis of 3,4,5,6-tetrahydrophthalic anhydride (THPA, **1**) in the presence of an organic base and transition metal ions (Co(II) and Mn(II)) under hydrothermal conditions has generated two different dicarboxylate ligands that are formally related by allylic rearrangement within the cyclohexene ring structure. The completeness of the rearrangement is dependent on the nature of the metal ions, producing distinctly different structures of the metal-ligand complexes. The co-existence of 1,2-chedc and 2,3-chedc in the same metal complex **2Mn** would lend strong support to the proposed mechanism. DFT calculation suggests S$_E$1 mechanism is operative via an OH$^-$/H$_2$O assisted process. This work thus offers a rare and well-investigated example of in situ ligand transformation under hydrothermal conditions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental and calculation procedures, crystallography and reaction mechanisms]. See DOI: 10.1039/b000000x/

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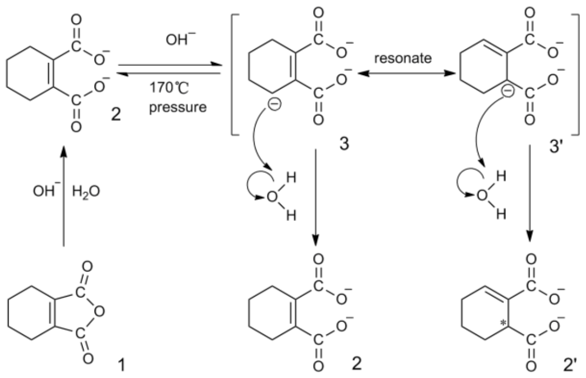

Allylic rearrangement was first observed in a hydrothermal reaction of cyclic dicarboxylic anhydride with different metal centres, which can be rationalised as S_E1 mechanism via the isolation of two resonated intermediates and DFT calculations.

Supporting Information for

Observation of allylic rearrangement in water-rich reaction

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1. General Experimental Section

Unless stated otherwise, all reagents and solvents were purchased commercially and used without further purification. Microanalyses (CHN) were carried out using an Elementar Vario-EL CHNS elemental analyzer.

Methods of Calculation

Full geometry optimization of all stationary points involving the cyclohexene-1,2-dicarboxylic acid, hydroxide ions and water molecules has been carried out using the density functional theory (DFT) method based on the hybrid of Becke's three-parameter exchange functional and the Lee, Yang, and Parr correlation functional (B3LYP) [S1- S3]. The 6-31+g* basis set is selected for hydrogen, carbon and oxygen and LANL2DZ is adopted to describe the metals of Mn and Co [S4]. Analytical frequency calculations are done at the same theoretical level, and the stationary points are distinguished as either energy minima (the number of imaginary frequencies (NIMAG =0) or transition states (NIMAG =1)). Furthermore, the intrinsic reaction coordinate (IRC) calculations [S5] are performed to confirm that the optimized transition states correctly connect the relevant reactants and products. All computations reported here are carried out using the GAUSSIAN 09 program suite [S6] and the electronic energies with the zero point energy correction are used to compute the potential energy surface.

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Optimized structures and 0 K energies (electronic and ZPE) in Fig. 3.

m1

E= -611.635300 hartree

C	-0.03467800	-0.67719200	-0.00362200
C	-0.26574700	0.65235300	-0.01430700
C	-1.14250900	-1.70986600	-0.01417200
H	-0.87282800	-2.49653100	-0.73062500

H	-1.16717100	-2.19791300	0.97315100
C	-2.51481800	-1.11312600	-0.35056100
H	-3.30050100	-1.83940500	-0.11042200
H	-2.57381400	-0.92420700	-1.43149500
C	-2.72938400	0.19982300	0.40822000
H	-2.67433000	0.00778200	1.48947400
H	-3.72847500	0.60578100	0.20946400
C	-1.66613700	1.23504400	0.01787300
H	-1.68645800	2.08053500	0.71426400
H	-1.89862000	1.66267300	-0.96889800
C	1.34211600	-1.28489200	-0.03617600
C	0.89223400	1.58356500	-0.08920100
O	2.06270300	1.26196300	-0.17962100
O	1.82858800	-1.79062700	-1.02457100
O	0.51332000	2.88991100	-0.06177800
H	1.33156700	3.41641400	-0.13065600
O	1.90752200	-1.34544000	1.19046800
H	2.78710300	-1.75583400	1.08142800

$OH^{-}(H_2O)_2$

E= -228.670379

O	-2.26873800	-0.40141900	0.03607400
H	-1.39475600	0.15732900	0.07735600
H	-1.95436700	-1.25014700	-0.30865100
O	0.00381500	0.87166600	0.07628100
H	-0.00415300	1.58541400	-0.57952200
H	1.30762400	0.04049700	-0.09124100
O	2.20344200	-0.49252000	-0.09946600
H	2.53750300	-0.35491100	0.79894400

m2

E= -840.325862

C	-0.67203600	0.48996600	-0.49086500
C	-1.20037200	-0.73478100	-0.24557400
C	0.70738400	0.70219500	-1.04870900
H	0.67000500	1.52871500	-1.77203100
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H	2.36688900	-0.40988000	-1.84624600
H	0.81900100	-0.76568700	-2.65141300
C	1.07905100	-1.75624000	-0.73788100
H	1.57467900	-1.54671500	0.21803300
H	1.53919100	-2.66558900	-1.14789000
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O	-1.95082400	2.42396000	-1.13637800
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H	-3.91022500	-2.07364600	0.74999800
O	-1.35249900	2.19299500	1.02509000
H	-1.84372500	3.03512400	1.06529300
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H	4.08376600	0.47181900	-0.14450700
H	5.08873200	-0.71456200	-0.32626000
O	3.00707500	0.99759900	0.90893500
H	3.34357500	1.80790200	1.32049800
H	2.53180300	-0.02279500	2.05206100
O	2.12760100	-0.66823800	2.73967900
H	1.22291100	-0.33980300	2.84774100

ts2/3

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C	0.78391600	0.36734700	0.52486800
C	1.57214900	-0.67568100	0.07689200
C	-0.49680900	0.21133200	1.16542500
H	-0.72699500	1.01430100	1.87445800
H	-1.45744800	0.45321800	0.23075500
C	-0.79907900	-1.19150100	1.68494400
H	-1.87680200	-1.29102800	1.87544700
H	-0.29062200	-1.38104600	2.64663000
C	-0.34582200	-2.23927600	0.65820000
H	-0.91921000	-2.09189900	-0.26701400
H	-0.56324200	-3.25635600	1.01548600
C	1.15477900	-2.11403100	0.34523100
H	1.40265600	-2.73918400	-0.52101900
H	1.74249900	-2.52456500	1.18288400
C	1.19933800	1.80077500	0.33126800
C	2.81296600	-0.40252100	-0.60909200
O	3.29029700	0.69281200	-0.91305800
O	1.76109000	2.48334800	1.16539400
O	3.52598100	-1.54691600	-0.93172600
H	4.32611900	-1.21228000	-1.37393200
O	0.74690300	2.32025400	-0.83980500
H	1.05741900	3.24484700	-0.86265000
O	-5.13850200	1.16743100	0.06476400
H	-4.15578300	1.19890400	-0.02963400
H	-5.33895200	0.33476500	-0.39776400
O	-2.45433600	0.62621700	-0.55881400
H	-2.07657400	1.16382700	-1.27376300
H	-3.41795100	-0.64911600	-1.15675400
O	-4.11388000	-1.33442200	-1.38928900
H	-3.93417400	-2.07285300	-0.78928300

m3

E= -840.327030

C	0.83068900	0.28472200	0.78872400
C	1.54808700	-0.64069900	-0.01998700
C	-0.07485100	-0.06890000	1.76998900
H	-0.47845200	0.69317700	2.43443300
H	-1.68955300	0.39004500	0.42318900
C	-0.31829600	-1.52540200	2.09511100
H	-1.35567300	-1.68071900	2.43081300
H	0.31867600	-1.85605800	2.93620500
C	-0.02756200	-2.41278600	0.87093700
H	-0.79293400	-2.22025600	0.10445800
H	-0.10640200	-3.47573900	1.14235700
C	1.36088500	-2.11851400	0.27259600
H	1.49762200	-2.70440500	-0.64406400
H	2.12915900	-2.48410900	0.97825100
C	1.02474100	1.76235200	0.58456000
C	2.45781000	-0.18064500	-0.99360000
O	2.74503600	0.99539100	-1.30191000
O	1.68198500	2.50721600	1.28087000
O	3.12748900	-1.20093300	-1.68740200
H	3.70120400	-0.70815700	-2.29902500
O	0.23821200	2.26520700	-0.42828000
H	0.49966600	3.19921600	-0.52835200
O	-5.25215700	0.66842800	-0.05142600
H	-4.35120600	0.99734900	0.12389500
H	-5.08434400	-0.02655700	-0.71574400
O	-2.26946400	0.78970300	-0.27482000
H	-1.65070700	1.42227400	-0.68593000
H	-3.02135900	-0.41550400	-1.40884300
O	-3.65783500	-1.00357100	-1.88288800
H	-3.33083400	-1.90284100	-1.73477400

m3’

E= -840.333222

C	1.57161200	0.30755200	-0.04340900
C	0.32416000	0.12651000	0.68070600
C	2.17709900	1.51436100	-0.22933800
H	3.09704900	1.56779700	-0.80664900
C	1.56030600	2.79048900	0.28612700
H	1.79276300	3.62515600	-0.39272500
H	1.99729400	3.06815700	1.26198100
C	0.03570100	2.63709000	0.43477100
H	-0.41148300	2.55978100	-0.56575300
H	-0.39580900	3.52963500	0.90931300
C	-0.32536200	1.38474200	1.24944800
H	-1.41713100	1.28041800	1.27981300
H	-0.01239300	1.54690700	2.29694900
C	2.23016100	-0.84181600	-0.73798500
C	0.03475400	-1.13803900	1.23425600
O	0.63608300	-2.22166500	1.11676800
O	3.40670400	-1.14990200	-0.67121200
O	-1.14232600	-1.15937300	2.03273800
H	-1.16711600	-2.08076800	2.34643300
O	1.39502100	-1.50211800	-1.60477000
H	1.90608000	-2.27003000	-1.91876800
H	-0.88178800	-0.18022900	-0.90480000
O	-3.95571000	1.20038500	-1.43177200
H	-3.09895800	0.93324000	-1.81148500
H	-4.07026300	0.54134400	-0.71818300
O	-1.44993700	-0.42139900	-1.69102100
H	-0.83466700	-0.96371100	-2.21099200
H	-2.83864500	-1.22144500	-0.56597000
O	-3.45016000	-1.18821300	0.19953300
H	-2.83291600	-1.08330100	0.95127500

ts3’/4

E= -840.326229

C	-1.38703700	0.46194100	-0.01885000
C	-0.14718500	-0.19321500	-0.52781400
C	-1.75771400	1.72086400	-0.34225300
H	-2.65749000	2.13100300	0.11209900
C	-0.94172900	2.60988600	-1.24356400
H	-0.98676200	3.64610000	-0.87712300
H	-1.38847300	2.63080000	-2.25323900
C	0.51677600	2.13171400	-1.32190900
H	1.02179000	2.34142600	-0.37108000
H	1.05578100	2.68794200	-2.10189500
C	0.58507900	0.62754400	-1.61169400
H	1.63207000	0.30972200	-1.66299500
H	0.14895500	0.43575300	-2.60679000
C	-2.22619800	-0.20705500	1.01808800
C	-0.31985000	-1.60665000	-0.86214600
O	-1.25190500	-2.35631500	-0.58199000
O	-3.43868300	-0.11384800	1.13295900
O	0.76292300	-2.13921500	-1.55200100
H	0.54286400	-3.08298900	-1.65192200
O	-1.49225500	-0.89872200	1.93340700
H	-2.14065900	-1.32406200	2.52312700
H	0.74032900	-0.19048100	0.47145000
O	3.13726400	2.17008600	1.70029900
H	2.54997300	1.36165000	1.62020100
H	3.97630800	1.87251300	1.31925600
O	1.70709600	-0.09947300	1.35960500
H	1.28788300	-0.43019300	2.16979200
H	2.88552000	-1.23194300	0.66889700

O	3.40507700	-1.85874300	0.09601800
H	2.76291600	-2.05755800	-0.60530000

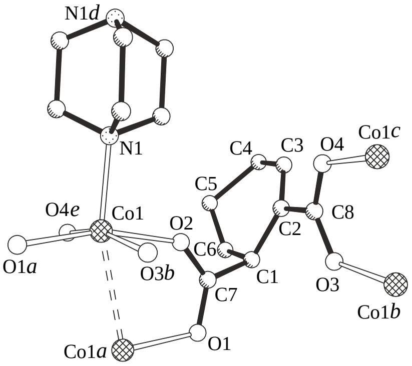
m4

E=- 840.328868

C	1.27205100	-0.66613200	0.00591900
C	0.19116300	0.32784000	-0.36714300
C	1.30800500	-1.92438900	-0.47076300
H	2.10491200	-2.57790400	-0.12002100
C	0.29214800	-2.49475300	-1.41875900
H	0.04769200	-3.52013600	-1.10632700
H	0.75567400	-2.59037400	-2.41681500
C	-0.97952600	-1.63776900	-1.48635000
H	-1.58754500	-1.80457200	-0.58966700
H	-1.58915800	-1.94086400	-2.34900400
C	-0.62929400	-0.15112500	-1.60066100
H	-1.54223400	0.44925800	-1.65790900
H	-0.05063100	0.02080200	-2.52272400
C	2.28952200	-0.31298200	1.02972800
C	0.76806400	1.68160800	-0.70229600
O	1.90724800	1.93197800	-1.05727300
O	3.32159400	-0.92227500	1.27028600
O	-0.16697900	2.67420400	-0.63949900
H	0.28908900	3.48923300	-0.91938200
O	1.94949100	0.79016200	1.75042700
H	2.67808800	0.93471500	2.38051000
H	-0.54033500	0.42234000	0.47124700
O	-3.18704000	-2.20629600	1.23547500
H	-2.77256200	-1.27123500	1.38574600
H	-4.09161700	-2.00607300	0.95380300
O	-2.18537800	0.17955200	1.48859300
H	-2.08897500	0.41560400	2.42378200
H	-2.96434400	1.40173300	0.70829900
O	-3.29600700	2.18641400	0.14999500
H	-2.46428400	2.57377300	-0.16361600

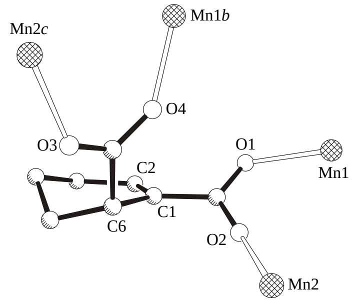
2. Syntheses

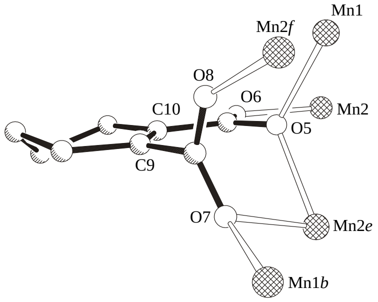
2.1 Synthesis of ${}^{2}_{\infty}$[Co^{II}(2,3-chedc)(DABCO)$_{0.5}$] (1Co)



$CoCl_2 \cdot 6H_2O$ (0.237 g, 1 mmol), THPA (0.168 g, 1 mmol), DABCO (0.112 g, 1 mmol) and 10 mL deioned water were mixed and stirred in the air for 10 minutes before transferred to a 15 mL Teflon-lined auto-clave and heated at 170 °C for 72 hrs. The reactants were then cooled to 100 ^{o} C in a rate of 5 ^{o}C / h. After keeping 12 hrs at 100 ^{o}C the bomb was further cooled to room temperature naturally. Dark red block crystals were collected. Yield: 75 % (calculated from $CoCl_2 \cdot 6H_2O$ used). Elemental analysis, calcd (%) for $C_{11}H_{14}CoNO_4$: C, 46.66; H, 4.98, N 4.95; Found: C, 46.78; H, 4.85; N, 4.83 %.

2.2 Synthesis of ${}^{2}_{\infty}$[Mn$^{II}_{2}$(1,2-chedc)(2,3-chedc)(H$_2$O)] (2Mn)





A mixture of $MnCl_2 \cdot 4H_2O$ (0.198 g, 1 mmol), THPA (0.168 g, 1 mmol), NaOH (0.080 g, 2.0 mmol) in a molar ratio of 1:1:2 in deionized water (15 ml) was quickly sealed in a 23-ml Teflon-lined autoclave and heated at 170 °C for 72 hrs to give colourless plate-like crystals of **2Mn** (yield 33 % based on THPA). Elemental analysis, $C_{16}H_{22}Mn_2O_9$, calcd.: C, 41.04; H, 4.74; found: 41.10; H, 4.69 %.

3. X-Ray Crystallography Data

Crystal data of **1Co** and **2Mn** were collected on a Bruker Apex CCD area-detector diffractometer by using MoKα (λ = 0.71073 Å) radiation. Absorption corrections were applied by using the multi-scan program SADABS [S7]. The structures were solved using direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [S8]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Data collection and structural refinement parameters are given in Table S1 and selected bond distances and angles are given in Table S2. CCDC-907607 and 907608 contains the crystallographic data that can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for **1Co** and **2Mn.**

	1Co	**2Mn**
Formula	$C_{11}H_{14}CoNO_4$	$C_{16}H_{22}Mn_2O_9$
F.w.	283.16	468.22
T (K)	288(2)	293(2)
Space group	$P2_1/n$	P-1 (No. 2)
a (Å)	6.3144(6)	7.5830(6)
b (Å)	20.2085(19)	9.8009(8)
c (Å)	9.4966(9)	13.5331(10)
α (°)	90	71.8910(10)
β (°)	106.0050(10)	86.0530(10)
γ (°)	90	71.7570(10)
V (Å^3)	1164.84(19)	907.46(12)
Z	4	2
D_c (g cm^{-3})	1.615	1.714
μ (mm^{-1})	1.475	1.439
Data collected/unique	6741 / 2245	9383 / 3555
R_1 (>2σ/all data)	0.0506 / 0.0547	0.0346 / 0.0380
wR_2 (>2σ/all data)	0.1351 / 0.1385	0.0958 / 0.0982
GOF (all data)	1.060	1.053
Residues (e Å^{-3})	-0.725 / 0.915	-0.859 / 0.537
CCDC No.	907607	907608

Table S2 Selected bond lengths (Å) and bond angles (°) for **1Co** and **2Mn**.

			1Co				
Co(1)-O(4)#1	2.026(2)	Co(1)-O(1)#2	2.029(3)	Co(1)-O(3)#3	2.031(2)	Co(1)-O(2)	2.077(3)
Co(1)-N(1)	2.113(3)	Co(1)#2⋯O2	2.805(3)	Co1⋯Co(1)#2	2.7572(9)		
C(1)-C(2)	1.512(4)	C(2)-C(3)	1.313(5)	C(3)-C(4)	1.510(7)	C(4)-C(5)	1.515(7)
C(5)-C(6)	1.512(7)	C(1)-C(6)	1.517(6)	C(1)-C(7)	1.516(5)	C(2)-C(8)	1.493(5)
O(4)#1-Co(1)-O(1)#2		94.64(13)	O(3)#3-Co(1)-O(2)		86.17(13)		
			2Mn				
Mn(1)-O(4)#1	2.0848(14)	Mn(1)-O(1)	2.0952(14)	Mn(1)-O(5)	2.1232(13)	Mn(1)-O(7)#2	2.1812(13)
Mn(1)-O(1W)	2.2039(16)	Mn(2)-O(3)#3	2.0949(14)	Mn(2)-O(2)	2.1318(14)	Mn(2)-O(8)#4	2.1338(14)
Mn(2)-O(6)	2.1620(14)	Mn(2)-O(5)#5	2.1674(13)	Mn(2)-O(7)#5	2.3843(13)		
C(1)-C(2)	1.323(3)	C(1)-C(7)	1.495(3)	C(1)-C(6)	1.510(3)	C(2)-C(3)	1.499(3)
C(3)-C(4)	1.526(4)	C(4)-C(5)	1.503(4)	C(5)-C(6)	1.536(3)	C(6)-C(8)	1.528(3)
C(9)-C(10)	1.336(3)	C(9)-C(14)	1.510(3)	C(10)-C(15)	1.488(3)	C(10)-C(11)	1.507(3)
O(4)#1-Mn(1)-O(1W)		78.65(6)	O(5)-Mn(1)-O(7)#2		96.66(5)		

Symmetry codes: for **1Co**: #1 x+1,y,z; #2 -x+1,-y,-z; #3 -x,-y,-z; #4 x-1,y,z; #5 -x+1,-y,-z+1; for **1'Co**: #1 x,-y,z ; #2 -x+1,-y,-z+2; #3 -x+1,y,-z+2; #4 -x,-y,-z+1; #5 -x,y,-z+1; #6 -x+1,y,-z+3; for **2Mn**: #1 -x+2,-y+1,-z; #2 -x+1,-y+2,-z; #3 -x+3,-y+1,-z; #4 x+1,y,z; #5 -x+2,-y+2,-z; #6 x-1,y,z.

[S7] Sheldrick, G. M. *SADABS 2.05*, University Göttingen, Germany, **2002**.
[S8] *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**.

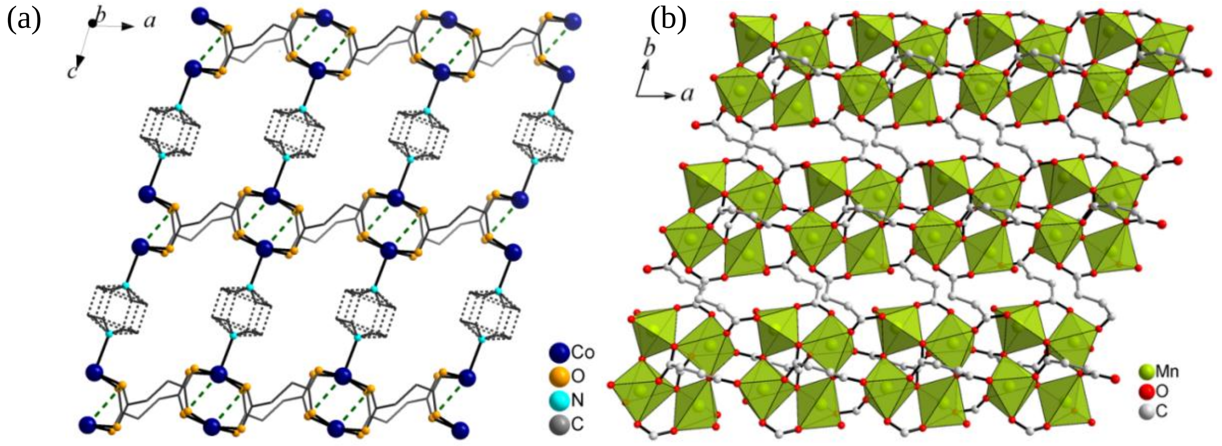


Fig. S1. The layer structures of **1Co** (a) and **2Mn** (b). The carboxylate-free skeleton carbons of the 2,3-chedc ligands were omitted for clarity in (b). Dotted lines: suspected (green) and disordered (gray) coordination bonds.

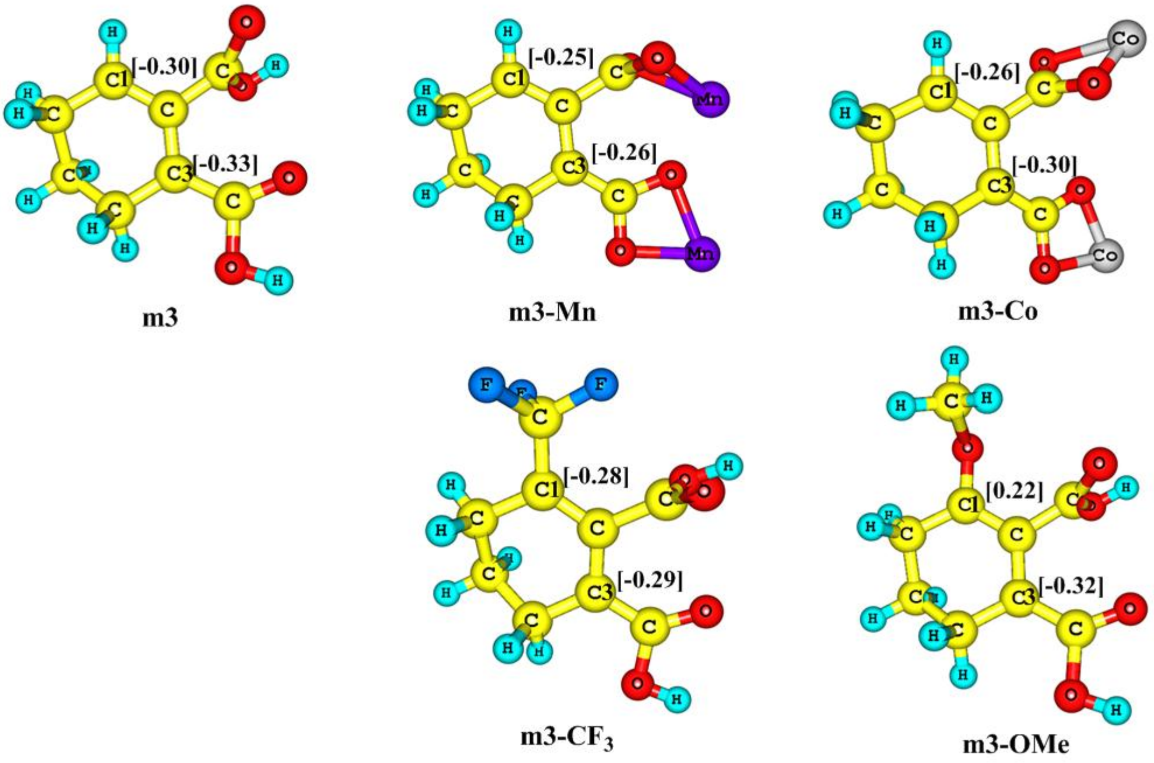


Fig. S2. Deprotonated structure **3** with no-metal (m3), **Mn** (m3-Mn), **Co** (m3-Co), electron withdrawing group substitution (m3-CF_3), and electron donating group substitution (m3-OMe). The structures are optimized with DFT and the NBO charges are labelled for C1 and C3. The water cluster is not included in the model.

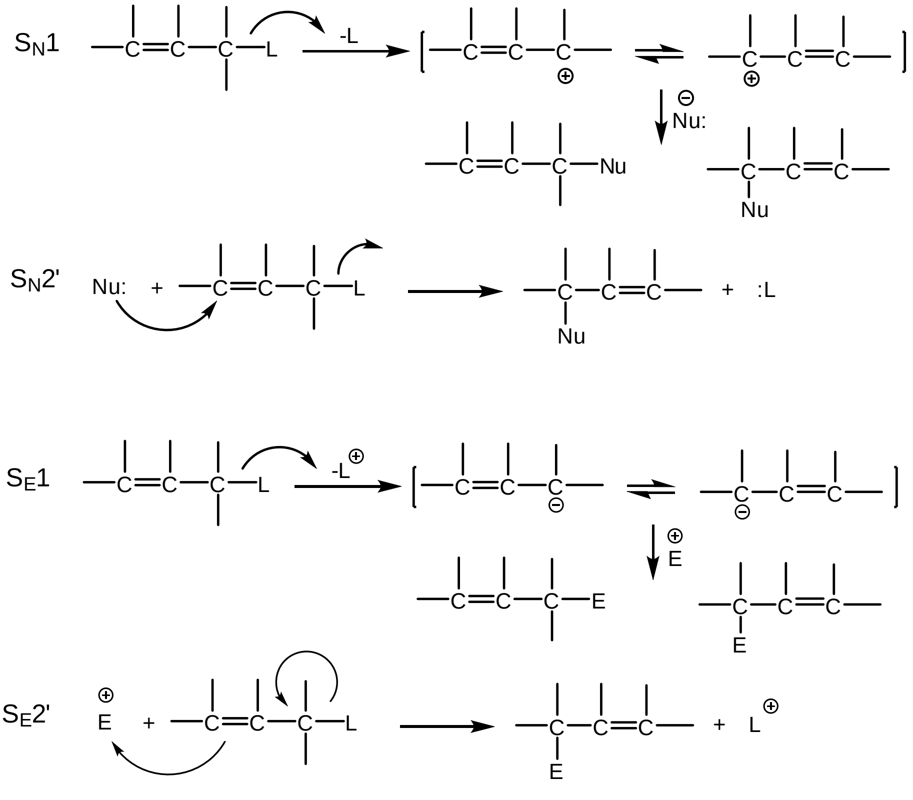
4. Mechanisms

Nucleophilic mechanism

Allylic rearrangements in the presence of nucleophiles can undergo *via* two mechanisms: S_N1 and S_N2' (Scheme S1). In S_N1 mechanism, a leaving atom or group is first removed, giving a resonance-stabilized allylic carbocation, which then attacks a nucleophile, forming two products: the original one and the rearranged one. When it undergoes the S_N2' mechanism, nucleophile attack the γ carbon, and simultaneously, the leaving atom or group is removed, completing the double bond migration, but with just one form.

Electrophilic Mechanism

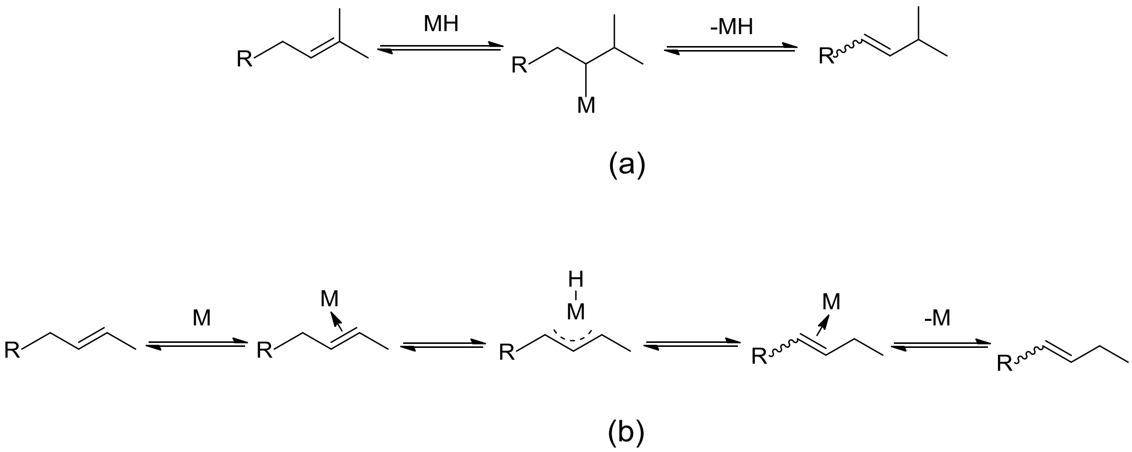
Electrophilic substitution also have two pathways, namely S_E1 and S_E2'. In the S_E1 mechanism, the leaving atom or group is removed to form a resonance-stabilized allylic carboanion. Followed by attacking an electrophile, the reaction eventually generates two resonated products (Scheme S1). Differently, in the S_E2' mechanism the π-bond attacks the electrophile while the leaving atom or group is removed simultaneously, generating only one kind of product.



Scheme S1. nucleophilic and eletrophilic pathways of double-bond re-arrangement.

Noble Metal Catalysed Mechanism

In the present of noble metal catalysts (complexes containing Pt, Rh, or Ru, or metal carbonyl catalysts), the double bond also can be obtained. This mechanism mainly contains two ways which are illustrated in the Scheme S2.



Scheme S2. Two pathways of double-bond re-arrangement catalyzed by noble metal complexes.