Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Observation of allylic rearrangement in water-rich reaction

Yuan-Chao Pang,[a,+] Xiufang Hou,[a,+] Lei Qin,[a] Chao Wu,*[,a] Wei Xue,[b] Yan-Zhen Zheng,*[,a] Zhiping Zheng[a] and Xiao-Ming Chen[b]

[a] Frontier Institute of Chemistry, Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an 710054, China

[b] School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

[+] These authors contributed equally to this work.

E-mail: zheng.yanzhen@mail.xjtu.edu.cn (Y.-Z. Zheng); chaowu@mail.xjtu.edu.cn (C. Wu)

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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[S2] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, Phys. Rev. A. 38 (1988) 3098–3100.

[S3] C. Lee, W.T. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B. 37 (1988) 785–789.

[S4] P. J. HAY, W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, J Chem. Phys. 1985 , 82(1) : 299- 310 .

[S5] C. Gonzalez, H. B. Schlegel, An improved algorithm for reaction path following, J. Chem. Phys. 90 (1989) 2154–2161.

[S6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, , J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.

Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox. Gaussian 09, Revision B.01. Gaussian, Inc., Wallingford CT, 2010.

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
H	1.39526300	1.03117400	-0.23202300
C	1.29631700	-0.56636900	-1.67762100
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
C	-0.41627100	-2.01163600	-0.49650700
H	-0.54791600	-2.68450000	0.35943500
H	-0.86106400	-2.53644400	-1.35735400
C	-1.42967100	1.76614500	-0.25642300
C	-2.58684200	-0.83921200	0.24645800
O	-3.36368500	0.07890400	0.46871200
O	-1.95082400	2.42396000	-1.13637800
O	-2.98955300	-2.13527300	0.43698900
H	-3.91022500	-2.07364600	0.74999800
O	-1.35249900	2.19299500	1.02509000
H	-1.84372500	3.03512400	1.06529300
O	4.75460400	0.05811300	-0.80460300
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

E= -840.320349

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

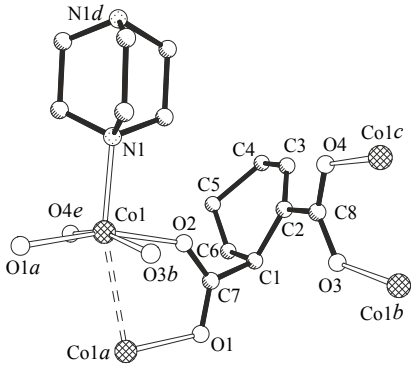
m4

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

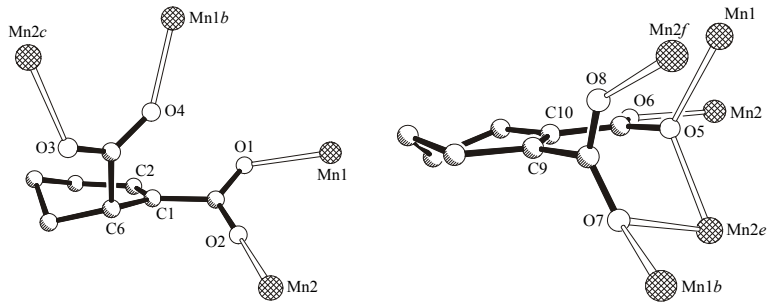
2. Syntheses

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_2O)] (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 %.

Electronic Supplementary Material (ESI) for Chemical Communications

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**.

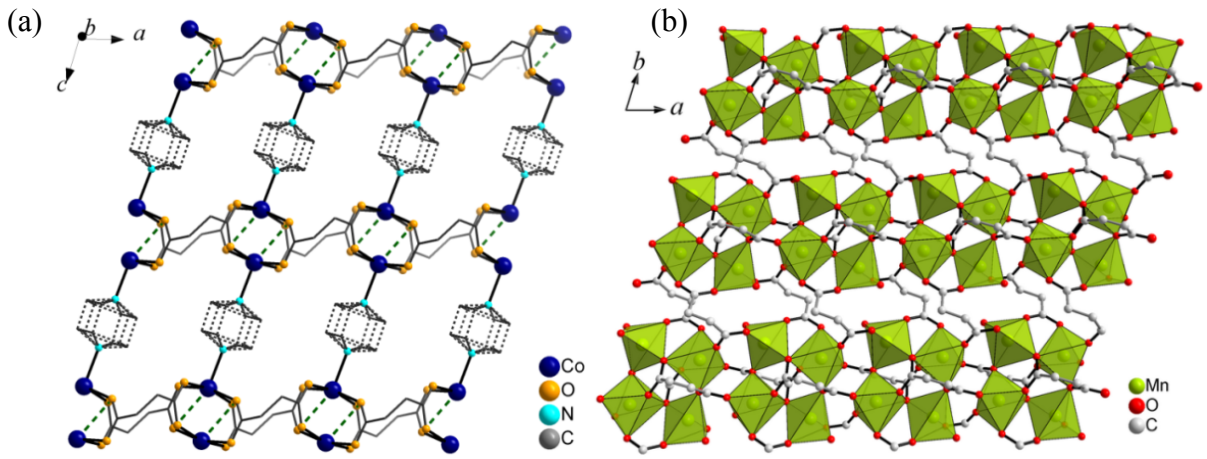


Fig. S1. The layer structures of **1Co** (a) and **2Mn** (b). The carboxylate-free skeleton carbons of the 2,3-chedc ligands were omitted for clarity in (b). Dotted lines: suspected (green) and disordered (gray) coordination bonds.

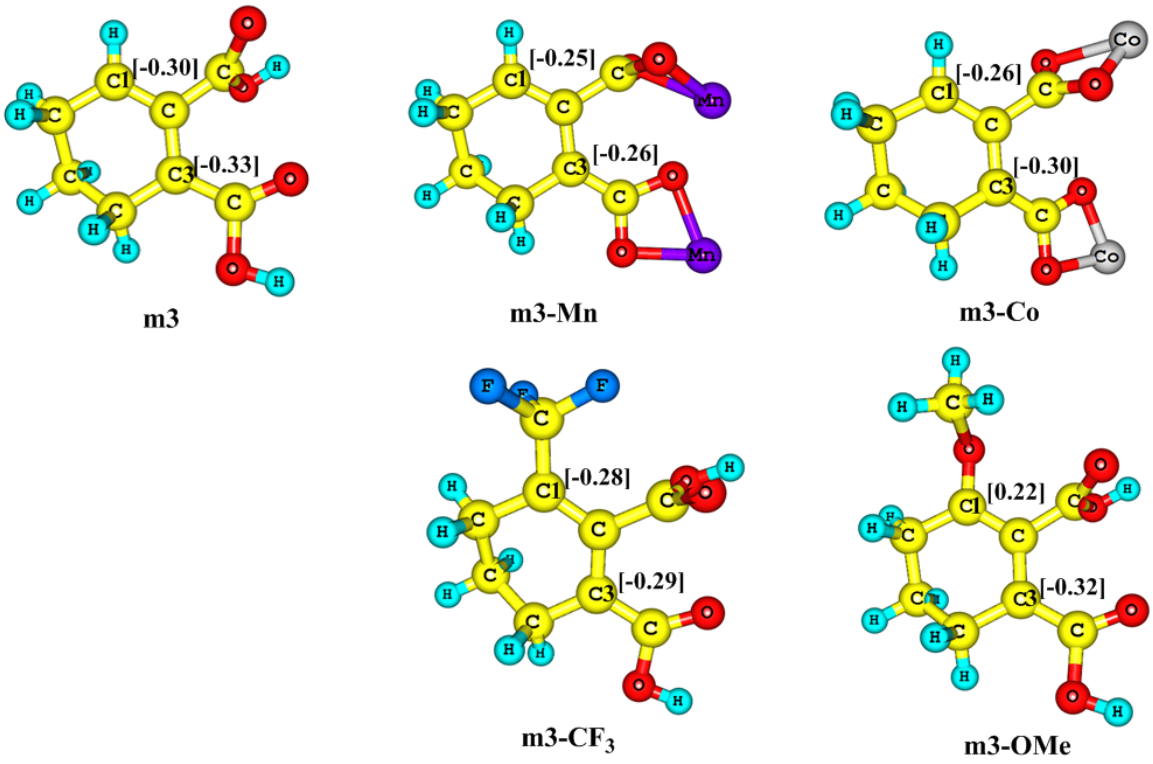


Fig. S2. Deprotonated structure **3** with no-metal (m3), **Mn** (m3-Mn), **Co** (m3-Co), electron withdrawing group substitution (m3-CF_3), and electron donating group substitution (m3-OMe). The structures are optimized with DFT and the NBO charges are labelled for C1 and C3. The water cluster is not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

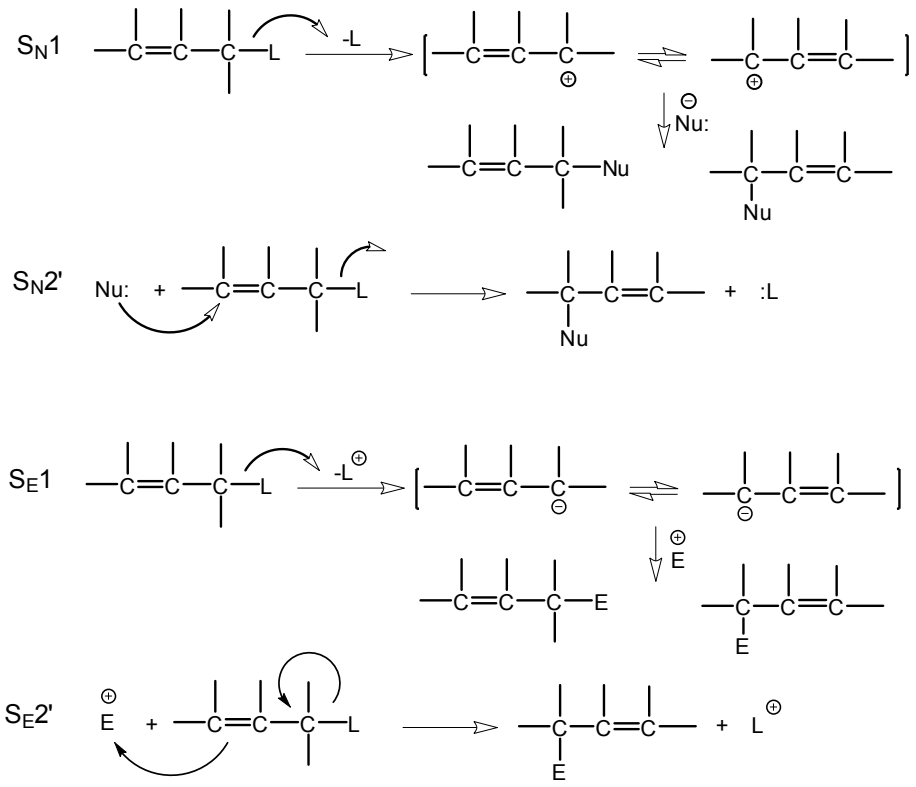
4. Mechanisms

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

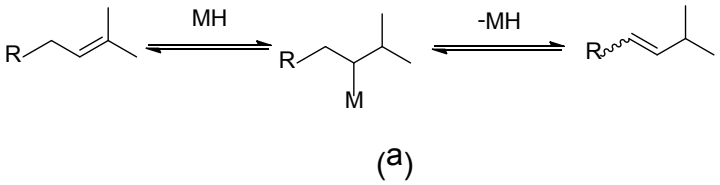
Electrophilic substitution also have two pathways, namely S_E1 and S_E2'. In the S_E1 mechanism, the leaving atom or group is removed to form a resonance-stabilized allylic carboanion. Followed by attacking an electrophile, the reaction eventually generates two resonated products (Scheme S1). Differently, 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.



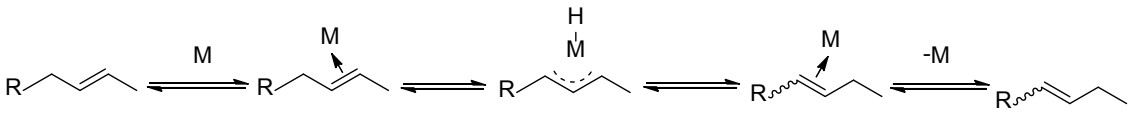
Scheme S1. nucleophilic and eletrophilic pathways of double-bond re-arrangement.

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.



(a)



(b)

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