Racemization Pathway for MoO$_2$(acac)$_2$ Favored over Ray–Dutt, Bailar, and Conte–Hippler Twists

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ABSTRACT: Chiral cis-MoO$_2$(acac)$_2$ racemizes via four pathways that agree with and extend upon Muetterties’ topological analysis for dynamic MX$_2$(chel)$_2$ complexes. Textbook Ray–Dutt and Bailar twists are the least favored with barriers of 27.5 and 28.7 kcal/mol, respectively. Rotating both acac ligands of the Bailar structure by 90° gives the lower Conte–Hippler twist (20.0 kcal/mol), which represents a valley−ridge inflection that invokes the trans isomer. The most favorable is a new twist that was found by 90° rotation of only one acac ligand of the Bailar structure. The gas-phase barrier of 17.4 kcal/mol for this Dhimba–Muller–Lammertsma twist further decreases upon inclusion of the effects of solvents to 16.3 kcal/mol (benzene), 16.2 kcal/mol (toluene), and 15.4 kcal/mol (chloroform), which are in excellent agreement with the reported experimental values.

Rationally designed catalysts capable of effecting enantioselective chemical transformations are crucial to satisfying the growing industrial demand for chiral fine chemicals. Despite the tremendous advances in asymmetric organocatalysis, as highlighted by the 2021 Nobel Prize in Chemistry, most catalysts used for the conversions of organic compounds are still transition-metal complexes with ligands coming from the ever-growing chiral pool. These chiral ligands are considered to be responsible for the transfer of chirality to the reaction product, but the elaborate syntheses and unpredictable enantioselectivity are limiting factors. An alternative is to solely use the stereogenicity of the metal center by the enantiomeric chelation of achiral ligands around the coordinating transition metal.

Octahedral chiral complexes are, in fact, known as far back as 1911 when Werner reported on [Co(en)$_3$]$_3^{3+}$ (en = ethylenediamine); $^5$ [Cr(en)$_3$]$_3^{3+}$, [Rh(en)$_3$]$_3^{3+}$, [Ir(en)$_3$]$_3^{3+}$, and [Pt(en)$_3$]$_4^{4+}$ were described shortly thereafter. Werner’s $D_{3d}$ symmetrical cobalt(III) complexes carrying three simple achiral bidentate ligands were revived recently by Gladysz et al., demonstrating their effectiveness as enantioselective catalysts. In 2003, Fontecave et al. introduced the term “chiral-at-metal” catalysis and showed modest enantioselectivity for the asymmetric transfer hydrogenation and asymmetric oxidation of sulfides using [Ru(dmp)$_2$(CH$_3$CN)$_2$]$_2^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline). $^8$ The field of chiral-at-metal catalysis was expanded majorly in the past decade by Meggers et al., who reported many different asymmetric catalytic reactions with high enantioselectivity using chiral rhodium(III) and iridium(III), $[M(tbpb)$_2$(CH$_3$CN)$_2]^+$ (M = Rh, Ir; tbpb = S-tert-butyl-2-phenylbenzoazole), $^7$ and recently with similar chiral iron(II) complexes. $^9$

The asymmetric Lewis acid transition-metal complexes, carrying two bidentate and two acetonitrile ligands, apparently have high energy barriers of racemization, which enable the catalysts to maintain their chiral integrity. However, retention of chirality for other transition-metal complexes is a priori not evident because of the configurational flexibility at the metal center. $^10$ Whereas such dynamics can be restricted by bi-, tri-, and tetradeinate ligands, racemization is of general concern in chiral-at-metal systems. The crux is to recognize and control the dynamic pathways.

Already half a century ago, in-depth topological studies by Muetterties revealed the complexity by which penta- and hexacoordinate systems racemize. $^12$ He also showed that the number of racemization pathways reduces with bidentate ligands. Illustrative is the reduction of 20 feasible permutations of a pentacoordinate system, which can be described in a Levi–Desargues graph, by introducing two bulky bidentate ligands. $^13$ These cause the energy barriers for Berry pseudorotation to increase and prohibit racemization, as is the case for silicate $[Si(pn)$_2$F]^- [pn = 2-(phenyl)naphthyl]$. $^14$ Octahedral complexes are subject to a far larger number of permutations, which also reduce upon chelation. Well-established racemization pathways for trischelate complexes are the Ray–Dutt $^{15}$ and Bailar $^{16}$ twists in which the chelating ligands undergo a C$_3$ rotation $^{17}$ via rhombic ($D_{3d}$ symmetry) and trigonal-prismatic ($C_{3v}$ symmetry) transition states, respectively (Figure 1). $^{18}$ Rarer pathways include the dancing-Bailar twist, $^{19}$ those with a bicapped tetrahedral structure, $^{20}$ and those invoking pentacoordination. $^{21}$ Besides Muetterties’ topological studies, little is known about the racemization pathways of octahedral complexes with two bidentate ligands, which is the subject of the present study that focuses on cis-MoO$_2$(acac)$_2$ (acac = acetylacetonate).

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cis-MoO$_2$(acac)$_2$ is an effective catalyst for epoxidizing olefins with peroxides, but we are not aware of asymmetric homogeneous catalysis with one of its enantiomers.$^{22}$ The solid-state structure has been reported for the racemic mixture$^{23}$ and for an enantiomer of a derivative.$^{24}$. Conte and Hippler determined by variable $^1$H NMR spectroscopy a modest activation energy $E_a$ of 16.9 kcal/mol for the racemization of cis-MoO$_2$(acac)$_2$ in benzene, 13.7 kcal/mol in chloroform, and 15.1 kcal/mol in toluene, indicating a small solvation effect.$^{24}$ These barriers are similar to those reported by the group of Wise in 1971.$^{25}$ SOGGA11-X/LANL2DZ +G** calculations by Conte and Hippler gave $E_a$ barriers of 26.7 and 27.2 kcal/mol for the Ray–Dutt and Bailar twists and a lower, but still sizable, barrier of 19.4 kcal/mol for a different pathway; the heights of the barriers were not affected by inclusion of the effect of solvents. The magnitudes of these barriers seem to indicate that the racemization of cis-MoO$_2$(acac)$_2$ cannot be attributed to the Bailar or Ray–Dutt twists and likely not to the twist suggested by Conte and Hippler. Therefore, in the context of the topological analysis of MX$_2$(chel)$_2$ systems, we felt that a theoretical study on the racemization pathways is in order.

The potential energy surface for the MoO$_2$(acac)$_2$ complex was examined with Gaussian 16, version B01,$^{26}$ using the hybrid meta-generalized-gradient-approximation functional oS97X-D,$^{27}$ which incorporates empirical dispersion terms and long-range interactions,$^{28,29}$ and the 6-31G(d) basis set for C, H, and O and LANL2DZ for Mo.$^{30}$ The reported absolute electronic energies for all optimized structures were estimated by single-point calculation with the 6-311+G(2d,p) basis set. Frequency and intrinsic-reaction-coordinate (IRC) calculations confirmed the nature of each transition structure.$^{30}$ The effect of solvation was estimated by single-point calculations with the polarizable continuum solvent model at 25 °C.$^{31}$

The geometries of $\Lambda$- and $\Delta$-cis-MoO$_2$(acac)$_2$, shown in Figure 2, have a distorted octahedral arrangement in which the planes formed by the acac ligands and metal center are each tilted by 10.8° from orthogonality with the MoO$_2$ plane. The Mo=O bonds of the MoO$_2$ fragment have a length of 1.692 Å and an angle of 104.6°. The two Mo–O bonds of each acac ligand are longer and unequal to each other, i.e., 2.019 Å (Mo–O$_{1a}$) and 2.252 Å (Mo–O$_{\text{trans}}$), because of the different chemical environments of the two acac oxygen atoms. The methyl groups of the acac ligands are eclipsed with the methine hydrogen atoms. The geometry of $\Lambda$-$\Delta$-cis-MoO$_2$(acac)$_2$ compares well with those of the reported X-ray crystal structures.$^{32}$

$\Delta$-MoO$_2$(acac)$_2$ ($C_{2v}$ symmetry), shown in Figure 2b, is a substantial 50.6 kcal/mol less stable than the cis isomer. It is then not surprising that no solid-state structure is known for this isomer. Moreover, geometry optimization with the extended basis set suggests it to be a transition structure ($C_{2v}$ symmetry) at a flat energy plateau with an imaginary frequency of a mere $-12$ cm$^{-1}$. The trans Mo=O bonds of its MoO$_2$ fragment are longer (1.731 Å) than those in the cis isomer and deviate substantially from linearity (140.0°), and both tilt toward one of the acac ligands, which has as a result longer Mo–O bonds (2.137 Å) than the other ligand (2.034 Å).

To understand the racemization of cis-MoO$_2$(acac)$_2$ and the potential role of the trans isomer, it is instructive to analyze their topological relationship. Muetterties showed that a metal complex with six different (monodentate) ligands has 30 octahedral isomers and 120 trigonal-prismatic isomers but that this reduces significantly for complexes with two symmetrical bidentate ligands, MX$_2$(chel)$_2$. Figure 3, adapted from the original study, gives the topological representation, showing the enantiomeric cis isomers at the base and the trans isomer at the apex of an isosceles triangle (open dots). The closed dots at the edges of the triangle are the trigonal-prismatic structures (Figure 3, right), embodying rearrangement of the octahedral structures.

Topological analysis gives three direct racemization pathways for cis-MX$_2$(chel)$_2$, each with a trigonal-prismatic transition structure (cis$_{\alpha}$, cis$_{\beta}$) and trans in Figure 3), complemented by a pathway via the trans isomer that involves a set of enantiomeric structures (d$I$ trans). We are unaware whether all of these racemization pathways have found solid footing in the literature. Consequently, we felt MoO$_2$(acac)$_2$ was ideal to verify topological analysis in the context of...
Figure 3. Topological representation of MX₂(chel)₂ with octahedral structures (open dots) and connecting trigonal-prismatic structures (closed dots) shown separately.

comparing the racemization barriers of the cis isomer with the reported experimental one.

The obvious places to start with are the established Ray–Dutt and Bailar twists for trischelating octahedral systems (Figure 1), which are represented respectively as cis₂ and cis₂ in Figure 3. Their corresponding C₂ᵥ-symmetric transition structures for MoO₂(acac)₂ (Figure 4) have relative energies of

![Image](https://doi.org/10.1021/acs.inorgchem.2c00824)

Figure 4. Ray–Dutt (top) and Bailar (bottom) transition structures for the racemization of cis-MoO₂(acac)₂.

a significant 27.5 and 28.7 kcal/mol, respectively. The structure for the Ray–Dutt twist has its MoO₂ unit (d₁Mo=O = 1.696 Å; ∠OMoO = 97.4°) bisecting both virtually planar acac ligands (d₂Mo=O = 2.128 Å), which have an intercept angle of 19.6°. In the Bailar transition structure, the MoO₂ unit (d₁Mo=O = 1.687 Å; ∠OMoO = 95.8°) is rotated by 90° and has a larger bisecting angle of 48.3° between the acac ligands (d₂Mo=O = 2.148 Å).

Next, we focus on the role of trans-MoO₂(acac)₂ in isomerization of the cis isomer and on how the d,l trans forms (Figure 3) are involved. The latter can be considered to result from the Bailar transition structure by 90° rotation of both acac ligands. Such a transformation gives indeed a transition structure (Figure 5) with a relative energy of 20.0 kcal/mol, akin to that reported by Conte and Hippler. The two planar acac ligands of the C₂ᵥ-symmetric structure lie in the same plane, with each having Mo–O bonds of 2.040 and

Figure 5. Conte–Hippler transition structure for the racemization of cis-MoO₂(acac)₂.

2.264 Å to the MoO₂ unit (d₁Mo=O = 1.693 Å; ∠OMoO = 117.2°). The IRC confirms that this transition structure is yet another structure for the racemization of cis-MoO₂(acac)₂ (see the Supporting Information) by opposite rotation of the acac ligands, but it still does not match the reported experimental value.

Further inspection of the C₂ᵥ-symmetric structure is revealing. Rotating the MoO₂ plane that bisects the two acac ligands by 90° and enlarging the O=Mo=O angle (117.2° → 140.0°) results in C₂ᵥ-symmetric trans-MoO₂(acac)₂ (Figure 2b). This rotation can be left- or right-handed so that the MoO₂ unit gets directed toward either one or the other acac ligand, which is in accordance with topological analysis (Figure 3). The high-energy trans isomer lies on a very flat high-energy plateau that allows for slight bending of its acac ligands. Despite the technical difficulties that this caused, we obtained an IRC that connects trans-MoO₂(acac)₂ by left- and right-handed rotation of the MoO₂ unit to the Conte–Hippler transition structure (Figure 5) and thus ultimately to Δ- and Λ-cis-MoO₂(acac)₂. Evidently, this transition structure is a valley–ridge inflection point that gives one cis-MoO₂(acac)₂ enantiomer when the IRC is followed in one direction, likely because of torque selectivity. The relationship is shown in a simplified manner in Figure 6.

Figure 6. IRC for trans-MoO₂(acac)₂.

The only remaining racemization pathway to consider is that of the trans form in Figure 3. This twist is readily conceived by rotating one of the chelates of cis₂ by 90° instead of both. Such a rotation of one acac ligand of the Bailar structure led, in fact, to the hitherto unknown transition structure shown in Figure 7. Tracing the IRC trajectory confirms that it represents a new racemization pathway for cis-MoO₂(acac)₂ (see Figure S1). The two planar acac ligands of the structure lie in the orthogonal planes, with one having two symmetrical d₁Mo=O bonds (2.176 Å) and the other two unsymmetrical bonds (2.108 and 2.120 Å) to the MoO₂ unit (d₁Mo=O = 1.687 Å);

Figure 7. Tracing the IRC for cis-MoO₂(acac)₂.
derived from readily available, inexpensive transition metals, which we are currently exploring.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c00824.

All computational details (PDF)

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**Author Contributions**

All authors discussed the results and contributed to the final manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Walsh, P. J.; Kozlowski, M. C. Fundamentals of Asymmetric Catalysis; University Science Books: Sausalito, CA, 2009.

(2) The Nobel Prize in Chemistry 2021 was awarded jointly to B. List and D. W. C. MacMillan “for the development of asymmetric organocatalysis”. [www.nobelprize.org/prizes/chemistry/2021/summary](http://www.nobelprize.org/prizes/chemistry/2021/summary).

(3) Illustrative for chiral phosphorus-based ligands are: (a) *Phosphorus(III) Ligands in Homogeneous Catalysis*: Design and Synthesis; van Leeuwen, P. W. N. M., Kamer, P. C. J., Eds.; Wiley, 2012. (b) *Phosphorus Ligands in Asymmetric Catalysis*: Börner, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008. (c) Guo, H.; Fan, Y. C.; Sun, Z.; Wu, Y.; Kwon, O. Phosphine Organocatalysis. *Chem. Rev.* 2018, 118, 10049–10293. (d) Grabulosa, A. P-Stereogenic Ligands in Enantioselective Catalysis; RSC Publishing: Cambridge, U.K., 2011. (e) Cabré, A.; Riera, A.; Verdaguer, X. P-Stereogenic Amino-Phosphines as Chiral Ligands: From Privileged Intermediates to Asymmetric Catalysis. *Acc. Chem. Res.* 2020, 53, 676–689.

(4) (a) Bauer, E. B. Chiral-at-metal complexes and their catalytic applications in organic synthesis. *Chem. Soc. Rev.* 2012, 41, 3153–3167. (b) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. Highly efficient molybdenum-based catalysts for enantioselective alkene metathesis. *Nature* 2008, 456, 933–937.
(c) Gong, L.; Chen, L.-A.; Meggers, E. Asymmetric Catalysis Mediated by the Ligand Sphere of Octahedral Chiral-at-Metal Complexes. *Angew. Chem., Int. Ed.* 2014, 53, 10868–10874.

(d) Fontecave, M.; Hamelin, O.; Menage, S. Chiral-at-metal complexes as asymmetric catalysts. In Chiral Dizialigands for Asymmetric Synthesis. *Top. Organomet. Chem.* 2005, 15, 271–288.

(e) Knight, P. D.; Scott, P. Predetermination of chirality at octahedral centres with tetradentate ligands: prospects for enantioselective catalysis. *Chem. Soc. Rev.* 2003, 32, 1245–1255.

(b) Zhang, L.; Meggers, E. Steering Asymmetric Lewis Acid and Pressure NMR Kinetic Investigations. *J. Am. Chem. Soc.* 2010, 132, 18127–18140.

(2) Van Der Boon, L. J.; Van Gelderen, L.; De Groot, T. R.; Lutz, M.; Slookweg, J. C.; Ehlers, A. W.; Lammertma, K. Stereomutation of pentavalent compounds. validating the Berry pseudorotation, redressing the Ugi’s turnstile rotation, and revealing the two- and three-gated tunnels. *J. Am. Chem. Soc.* 2010, 132, 18127–18140.

(16) Bailar, J. C. Some problems in the stereochemistry of coordination compounds: Introductory lecture. *J. Inorg. Nucl. Chem.* 1958, 8, 165–175.

(17) (a) Casanova, D.; Cirera, J.; Llunell, M.; Alemany, P.; Avnir, D.; Alvarez, S. Minimal Distortion Pathways in Polyhedral Rearrangements. *J. Am. Chem. Soc.* 2004, 126, 1755–1763. (b) Amati, M.; Lelj, F. Competition between Bailar and Ray-Dutt paths in conformational interconversion of tris-chelated complexes: a DFT study. *Theor. Chem. Acc.* 2008, 120, 447–457.

(18) (a) Davis, A. V.; Firman, T. K.; Hay, B. P.; Raymond, K. N. d-Orbital Effects on Stereoelectronic Non-Rigidity: Twisted TiV Intramolecular Dynamics. *J. Am. Chem. Soc.* 2006, 128, 9484–9496.

(b) Rikkou, M.; Manos, M.; Tolis, E.; Sigalas, M. P.; Kabanos, T. A.; Keramidas, A. D. NMR and theoretical investigations on the structures and dynamics of octahedral bis (chelate) dichloro VIII compounds isolated by an unusual reduction of non-oxo VIV species. *Inorg. Chem.* 2003, 42, 4640–4649.

(19) Ashley, D. C.; Jakubikova, E. Ray-Dutt and Bailar Twists in Fe(II)-Tris (2, 2′-bipyridine): Spin States, Sterics, and Fe–N Bond Strengths. *Inorg. Chem.* 2018, 57, 5585–5596.

(20) Hoffmann, R.; Howell, J. M.; Rossi, A. R. Bicapped tetrahedral, trigonal prismatic, and octahedral alternatives in main and transition group six-coordination. *J. Am. Chem. Soc.* 1976, 98, 2484–2492.

(21) Foreman, M. R. S. J.; Hill, A. F.; White, A. J. P.; Williams, D. J. Hydrotris(methimazolyl)borato Alkylidyne Complexes of Tungsten. *Organometallics* 2003, 22, 3831–3840.

(22) (a) Annesi, C.; Caputo, D.; D’Accol, L.; Fusco, C.; Nacci, A.; Romaniello, M.; Tucci, G.; Giannini, G. Dioxygen-bridged (VI) Complexes with Salicylaldehyde Ligands: Synthesis, Structure, and Catalysis in the Epoxidation of Olefins under Eco-Friendly Conditions. *Eur. J. Inorg. Chem.* 2019, 2019, 221–229. (b) Korstanje, T. J.; Volker; Lutz, M.; Jastrzebski, J. T.; Klein Gebbink, R. J. Synthesis, Characterization, and Catalytic Behavior of Dioxygenolymogen Complexes Bearing AcAc-Type Ligands. *Eur. J. Inorg. Chem.* 2013, 2013, 2195–2204. (c) Shen, Y.; Jiang, P.; Wai, P. T.; Gu, Q.; Zhang, W. Recent progress in application of molybdenum-based catalysts for epoxidation of alkenes. *Catalysts* 2019, 9, 31.

(d) Kühn, F. E.; Santos, A. M.; Abrantes, M. Mononuclear Organomolybdenum (VI) Dioxo Complexes: Synthesis, Reactivity, and Catalytic Applications. *Chem. Rev.* 2006, 106, 2455–2475. (e) Barlan, A. U.; Basak, A.; Yamamoto, H. Enantioselective Oxidation of Olefins Catalyzed by a Chiral Bishydroxamic Acid Complex of Molybdenum. *Angew. Chem., Int. Ed.* 2006, 45, 5849–5852.

(23) (a) Kanemaru, B.; Penavic, M.; Prou, C. K. Dioxobis(2,4-pentanedionato)molybdenum(VI), [CH3H2ChoO2]2, *Cryst. Struct. Commun.* 1973, 2, 41–44. (b) Krasochna, O. N.; Sokolova, Yu. A.; Atovmyan, L. O. Crystal and Molecular Structures of Molybdenum bis-Acetylacetonate, MoO2(CH3acac)2, *Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.)* 1975, 16, 696–698. (c) Johnston, D. H.; King, C.; Seitz, A.; Sethi, M. Bis(2,4-dioxopentan-3-ido-J2O0,000)dioxo-molybdenum(VI): a redetermination. *JUCRData 2021*, 6, x10778.

(24) Conte, M.; Hippler, M. Dynamic NMR and quantum-chemical study of the stereochemistry and stability of the chiral MoO2(acac)2 complex in solution. *J. Phys. Chem. A* 2016, 120, 6677–6687.
Craven, B. M.; Ramey, K. C.; Wise, W. B. Lability and Stereochemistry of Dioxobis(2,4-pentanedionato)molybdenum (VI). Inorg. Chem. 1971, 10, 2626−2628.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 09, R. A.; Gaussian 16, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009 and 2016, Vol. 121, pp 150−166.

Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom−atom dispersion corrections. Phys. Chem. Chem. Phys. 2008, 10, 6615−6620.

Minenkov, Y.; Singstad, Å.; Occhipinti, G.; Jensen, V. R. The accuracy of DFT-optimized geometries of functional transition metal compounds: a validation study of catalysts for olefin metathesis and other reactions in the homogeneous phase. Dalton Trans. 2012, 41, 5526−5541.

(a) Couty, M.; Hall, M. B. Basis sets for transition metals: Optimized outer p functions. J. Comput. Chem. 1996, 17, 1359−1370.
(b) Yang, Y.; Weaver, M. N.; Merz, K. M. Assessment of the "6-31+G* + LANL2DZ" Mixed Basis Set Coupled with Density Functional Theory Methods and the Effective Core Potential: Prediction of Heats of Formation and Ionization Potentials for First-Row-Transition-Metal Complexes. J. Phys. Chem. A 2009, 113, 9843−9851.
(c) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 1985, 82, 270−283.

Gonzalez, C.; Schlegel, H. B. An improved algorithm for reaction path following. J. Chem. Phys. 1989, 90, 2154−2161.

(a) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. J. Phys. Chem. A 1998, 102, 1995−2001.
(b) Barone, V.; Cossi, M.; Tomasi, J. Geometry optimization of molecular structures in solution by the polarizable continuum model. J. Comput. Chem. 1998, 19, 404−417.
(c) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. J. Comput. Chem. 2003, 24, 669−681.

Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. Torquoselectivity in the Electroyclic Conversion of Benzocyclobutenes to O-Xylylenes. J. Am. Chem. Soc. 1992, 114, 1157−1165.