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Metal-to-Metal Distance Modulation by Ligand Design: A Case Study of Structure-Property Correlation in Planar Chiral Cyclophanyl Metal Complexes

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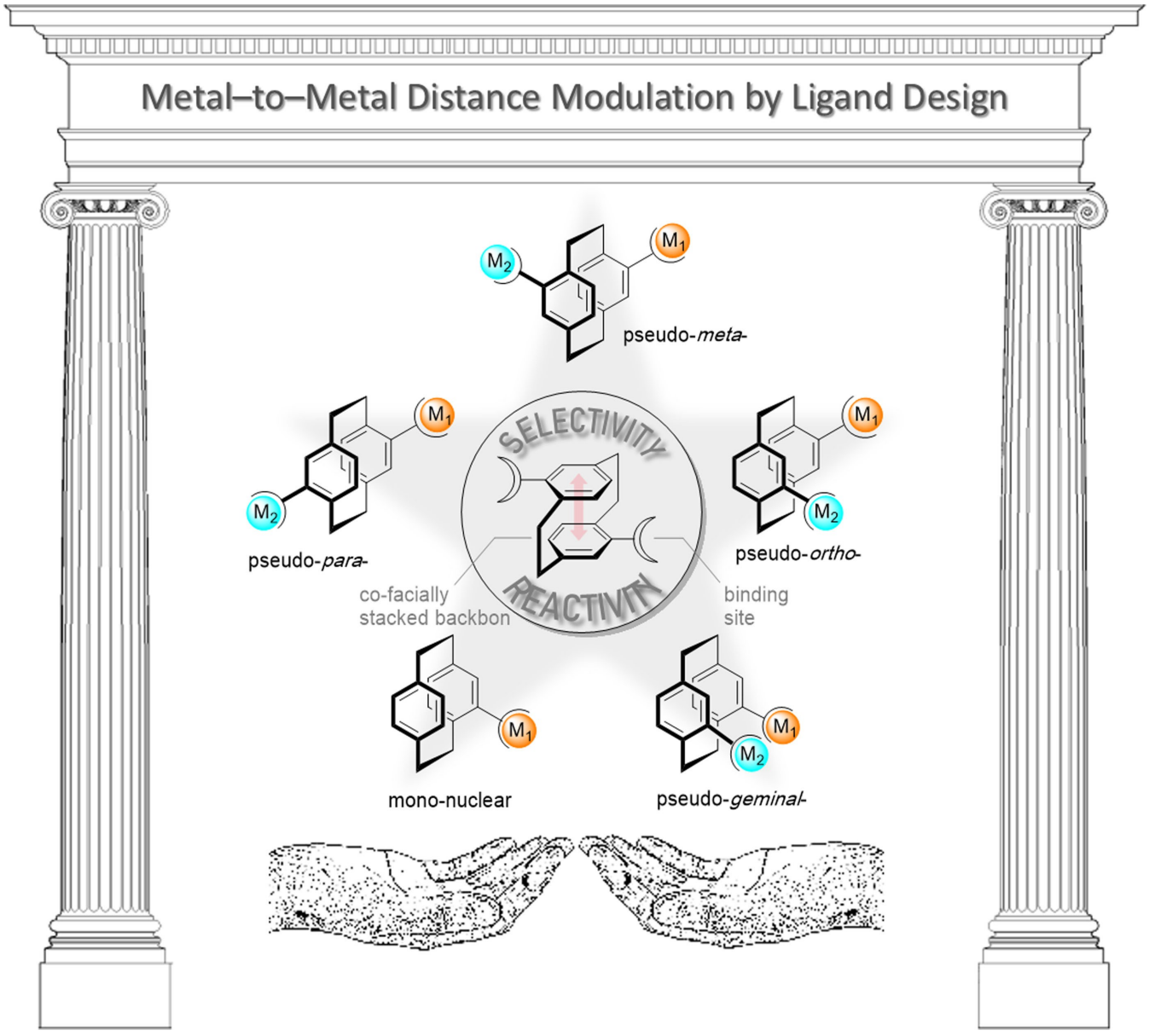

Abstract: Multinuclear metal complexes have seen tremendous progress in synthetic advances, their versatile structural features, and emerging applications. Here, we conceptualize Metal-to-Metal distance modulation in cyclophanyl metal complexes by bridging ligand design employing the co-facially stacked cyclophanyl-derived pseudo-*geminal*, -*ortho*, -*meta*, and -*para* constitutional isomers grafted with N-, O-, and P- containing chelates that allow the installation of diverse (hetero)metallic moieties in a distance-defined and spatially-oriented relation to one another. Metal-to-Metal distance modulation and innate transannular "through-space" π–π electronic interactions via the co-facially stacked benzene rings in cyclophanyl-derived complexes as well as their specific stereochemical structural features (element of planar chirality) are crucial factors that contribute to the tuning of structure-property relationships, which stand at the very center from the perspective of cooperative effects in catalysis as well as emerging material applications.

1. Introduction

Controlling the electronic coupling of individual transition metal centers as a function of their interatomic separation, relative orientation, and charge over sub-nanometer length scales has been a long-standing aspiration and research objective in fields ranging from spintronics to catalysis and optoelectronics.[1] A fundamental understanding of the electronic structure of small multinuclear metal complexes, their structure-property relationship and dependence on metal centers separation (relative orientation and charge) enables cooperative effects to be precisely tuned which could ultimately translate into their catalytic, magnetic, and optical properties.[2]

Inspired by precise control and efficiency of metalloenzymes evidenced in biological systems that possess more than one metal center (e.g., the homobimetallic catechol oxidase (Cu–Cu);[3] methane monooxygenase (Fe–O–Fe);[4] (Mn–Mn) containing arginase;[5] or heterobimetallic metalloenzymes phosphatase (Fe–Zn);[6] and CO dehydrogenase (Ni–Fe),[7] synthetic chemists by mimicking biological principles as a model have prepared a diverse library of multinuclear complexes that leverage metal-metal cooperativity.[8] By identifying different classes of homo- and heterometallic complexes (for instance, A_2, AB, ABC, AB_2, and A_3, where A, B, and C designate different types of metal atoms bound through bridging ligands as depicted in Figure 1), an outstanding progress has been made addressing synthetic, catalytic, magnetic, optical, and other physico-chemical properties.[9] Using appropriate bridging structures, a large number of bi-, tri-, and multinuclear complexes with varying degrees of Metal-to-Metal (M-to-M) interaction, based on the distance between the metal centers, have been synthesized. Most complexes contain transition metal sites known for their catalytic activity in synthetic transformations, for instance, Rh: in hydrogenation, hydroaminomethylation and cyclopropanation; Fe, Ru, Ir: transfer hydrogenation; Au: hydroamination; Pd, Cu: decarboxylative coupling; to name a few are well documented.[10]

Installing multinuclear moieties together on a single ligand scaffold can allow each to perform functions and/or enhance the existing efficiency of individual metal centers. This can lead to advantageous "cooperative effects" that might not be attainable with the individual metal centers.[11] Tuning multinuclear metal complexes, among various contributing factors based on the nature of the metal type, oxidation state, and coordination capabilities, M-to-M distance modulation has been a promising approach for identifying and optimizing structure-property relationship from the perspective of cooperative effects.[12]

Ligand design is of utmost relevance in investigating structure-property relationships and stands at the center from the application perspectives of metalloarenes.[13] Structural features of the bridging ligand such as flexibility or rigidity, steric, electronic effects, spatial orientation, and systematic variation of M-to-M distances to comprise novel functionalities

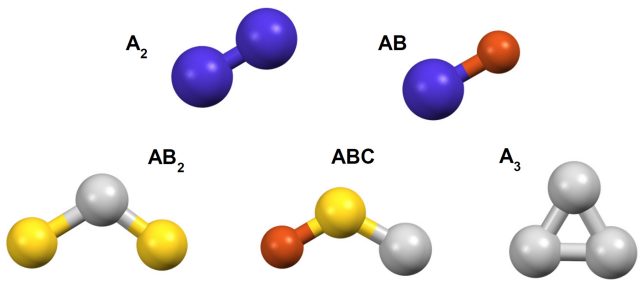

Figure 1. Types of metal combinations in complexes (reproduced from SFB/TRR 88 resources; Copyright 2018 3MET).

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are crucial contributing factors.[14] A careful selection of the ligand with selected arrangements of donor atoms and geometries allows precise M-to-M distance modulation. Despite the tremendous progress, positioning multiple metal centers in a predefined spatial separation, relative orientation, and electronic environment to achieve optimal interactions remains an interesting synthetic challenge. This concept article based on our recent advances and investigations on M-to-M distance modulation by ligand design in the context of structure-property relationship in cyclophanyl metal complexes could be of particular interest to synthetic and structural chemists aiming to work in the areas of cyclophane chemistry, focusing on the design and development of new heterometallic catalysts. We also believe this will inspire and aid in designing and understanding M-to-M interactions in metal complexes for emerging applications.

2. Why Cyclophanyl-derived Ligands?

The general term "cyclophane" could be coined to name any small or larger cyclic structure containing aromatic ring(s); hence a structurally diverse library of molecules can be referenced as cyclophanes. This report is confined to present a case study of the smallest stable co-facially stacked constrained cyclophane, that is [2.2]paracyclophane-derived complexes, focusing on M-to-M distance modulation and their structure-property relation. Mononuclear cyclophanyl complexes in which the planar chiral [2.2]paracyclophane moiety is instrumental for catalytic applications are reviewed in a tutorial,[15] and cyclophanyl-derived complexes containing a metal-metal (M–M) direct covalent bond, for instance, paddlewheel dirhodium $Rh_2(S_p\text{-PCP})_4$ binuclear complexes[16] are beyond the mandate of this report.

[2.2]Paracyclophane (cyclophanyl; PCP) is a co-facially stacked prochiral scaffold that features unusual characteristics caused by the transannular π-π electronic interactions of the benzene rings stacked in close proximity and exhibits unique stereochemical features (planar chirality) on selective functionalization.[17] The modular nature of PCP core fulfills some critical requirements for an ideal ligand. Rigidity, stability, planarity, π-stacking, and electronic communication via through-space and through-bond pathways within the PCP are interesting aspects for consideration in metal complexes. Using carefully chosen transformations, different functional groups can be selectively incorporated on either benzene rings, that is, mono-, and differently functionalized PCP regioisomers including pseudo-*para*, -*ortho*, -*meta*, and -*gem*, derivatives depicted in Figure 2 can be synthesized. The prefix pseudo (ps) is used if the two substituents are positioned on different decks of the PCP scaffold.

PCP with up to sixteen precisely defined substituents in fixed positions allows the tuning of geometrical relationships between the substituents. Metals can be linked to the PCP scaffold by cyclometallation, or by grafting various coordination-capable ligands first followed by cyclometallation.[18] Synthetic strategies in combination with versatile named

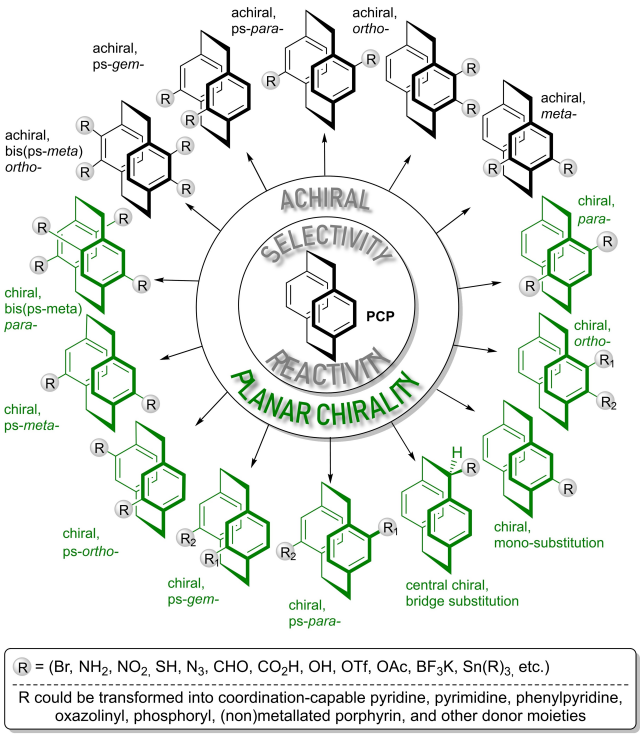

Figure 2. Common substitution patterns of mono-, di-, and tetra-substituted PCP with their stereochemical descriptions and their post-synthetic transformations

reactions, for instance, the Suzuki-Miyaura, Mizoroki-Heck, Stille-Migita, Hiyama, Kumada-Corriu, Negishi, Buchwald-Hartwig, and Sonogashira-Hagihara coupling reactions, can build PCP-derived bridging ligands in an enormous variety of geometry and sizes bearing coordination-capable different moieties including but not limited to, pyridine, phenylpyridine, pyrimidine, oxazolyl, phosphoryl, (non)metallated porphyrin, and other diverse *N*-, *O*-, *P*- containing ligand derivatives that can form complexes of distinct architectures and properties.[19]

The installation of (hetero)bimetallic moieties to the PCPs scaffold could bring them a well-defined and spatially-oriented relation to one another where M-to-M distance modulation can be studied. The structure-activity relationship, particularly through-space electronic communication and cooperative effects can be examined by employing cyclophanyl-derived constitutional isomers. In the context of π-electronic communication through-space via the co-facially stacked benzene rings and through-bond pathways, various constitutional isomers of electroactive ruthenium (Ru) and ferrocenyl-substituted (Fc) cyclophanyl complexes have been investigated. Comparing to non-PCP analogs of phenyl or dibenzocycloheptene-derived diruthenium complexes and transannular communication in PCP-containing binuclear rhenium (Re) complexes have been examined where electronic through-space coupling via stacked benzene rings was more efficient than a through-bond pathway (Figure 3).[20] Platinum-based organometallic polymers,[21] PCP-derived molecular junctions in oligo(phenylenevinylene)s,[22] and other studies proving though-space charge transfer

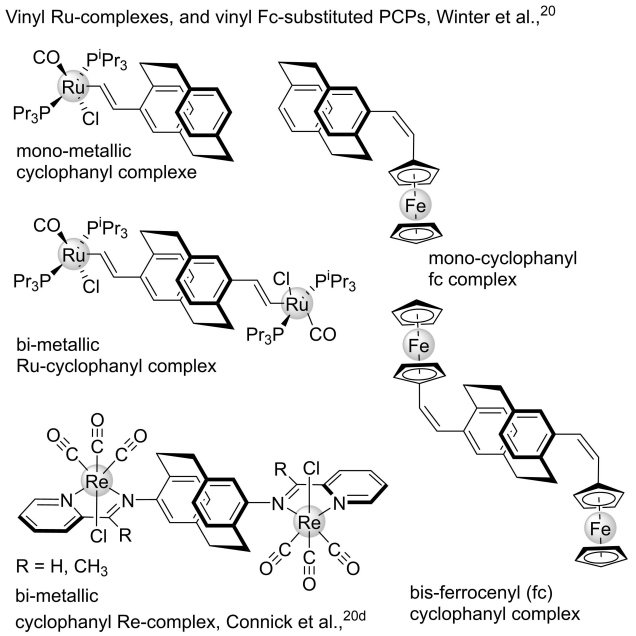

Figure 3. Electron delocalization via through-space and through-bond pathways in pseudo-*para* substituted cyclophanyl Ru, Re, and Fc complexes.

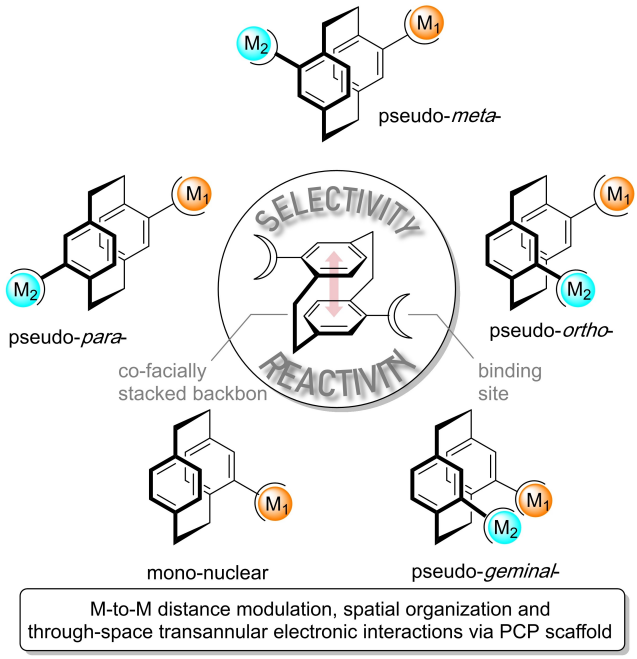

Figure 4. Heterobimetallic cyclophanyl complexes with varying M-to-M distances in spatial organization.

between the two cyclophane decks (interchromophore delocalization) are well documented in literature.[23]

Our research group and others have investigated PCP-derived metal complexes from various application perspectives, including developing PCP-based planar chiral ligands and catalysts employed in asymmetric transformations.[24] Cyclophanyl-derived model homobimetallic digold(I) complexes with varying intramolecular Au–Au distances based on diphosphane ligands of PhanePhos, xyl-PhanePhos, and Ph_2-GemPhos have been demonstrated .[25] By single crystal X-ray diffraction, the – distance in pseudo-geminal (2.98 Å) and pseudo-ortho (5.23 Å) position, as well as the respective P–P distances of 4.068 Å and 5.014 Å, for the corresponding precursor diphosphane ligands were determined. M-to-M distance modulation in (hetero) bimetallic Au/Ru complexes have been realized by combining a phosphinyl binding site to coordinate catalytic gold(I) component together with C,N-chelating 2-phenylpyridine moiety for the incorporation of a photon-capturing Ru(bpy)$_2$ppy moiety as a photocatalyst where the PCP provides a central scaffold (Figure 4). Their synthetic applicability was examined in a visible-light mediated arylative Meyer-Schuster rearrangement, transforming propargyl alcohols into α,β-unsaturated enones.[26] The photophysical and electronic ground-state properties of the Au/Ru heterobimetallic cyclophanyl complexes supported by ultrafast transient photodissociation spectroscopy in gas-phase and TD-DFT calculations evidenced M-to-M interactions and transannular communication. In this particular setup, a systematic reduction in M-to-M distance between the Au(I) and Ru(II) moieties plays a crucial role, ultimately caused a reduction in product yield.

Other recent examples include distance-modulated dinuclear cycloruthenation complexes using cyclophanyl-derived N-donor ligands (pyridyl, pyrimidyl, and oxazolinyl) that hold the two Ru-metals selectively either at only one or at both decks with varying M-to-M distances and spatial orientation.[27] Spacer groups, for instance, multiple pyridyl units, increase chelating ability and thus enable higher stability. Bidentate bipyridine (bpy), phenanthroline, bisoxazoline (box), tridentate terpyridine (tpy), tetradentate quaterpyridine (qpy), and cyclometallated phenylpyridine can be constituted to tailor the cavity shapes, sizes, and geometries which allow tuning of specific coordination environment for one or more metals, and M-to-M distance modulation at different-length scale.[28] Similarly, PCP–porphyrin conjugates as scaffolds allow convenient access to modular and fixed-distance bimetallic Cu/Zn complexes.[29] Some representatives of cyclophanyl-derived structures are shown in Figure 5.

Other cyclophanyl complexes, such as dithia[3.3] paracyclophane-bridged bimetallic ruthenium complexes (similar to PCPs), have also been prepared which share similar features arise from modular variations of the M-to-M distances. Spectroelectrochemical experiments supported by theoretical calculations have shown the influence of transannular π–π interactions on their electronic properties.[30]

Beyond simple small metal complexes, PCP bearing coordination-capable moieties as ligands in combination with metal precursors have also been demonstrated in the development of a new class of materials by self-assembly: namely metal–organic cages,[31] 1D organometallic polymer containing PCP,[32] and extended multinuclear 3D coordination frameworks that exhibit highly ordered periodic arrangements with confined and distance-defined metallic nodes.[33] Such extended multinuclear coordination-driven framework materials are ideal candidates to be used as heterogenous catalysts with confined reactivity.

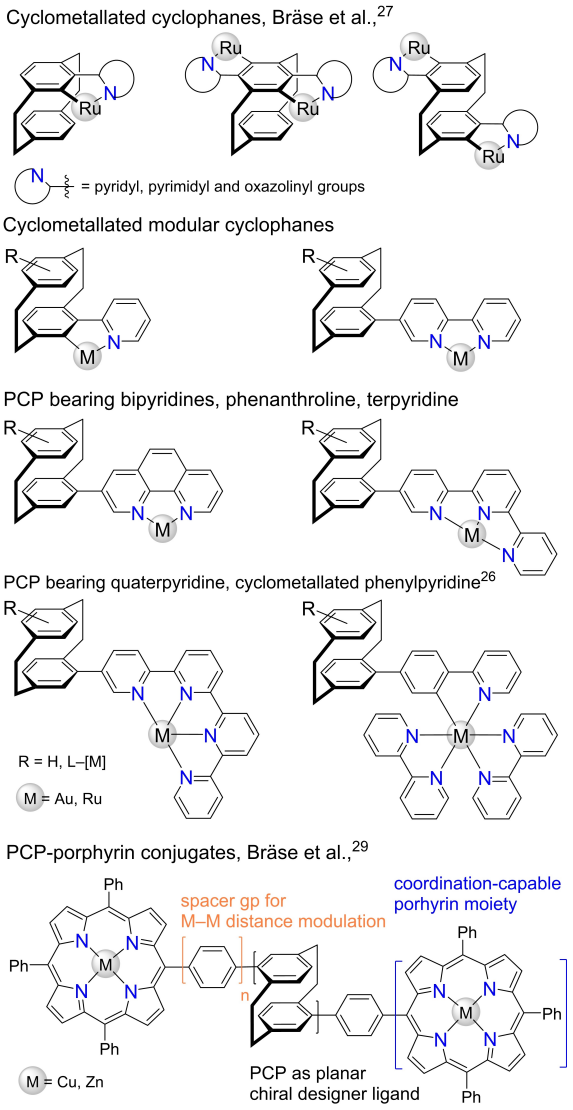

Figure 5. Model cyclophanyl complexes with varying M-to-M distances and coordination environments modulated via coordination-capable substituents

study, model heterometallic cyclophanyl complexes were examined for their synthetic applicability in a visible-light mediated arylative Meyer-Schuster rearrangement focused on exploring the structure-properties relation and cooperative effects in photoredox catalysis. Steric effects, electronic parameters can influence the chemical reactivity, and a systematic variation in M-to-M distance between the Au(I) and Ru(II) moieties plays a crucial role. This demonstration inspire the development of more efficient systems by merging transition metals and photocatalysis to enable chemical synthesis employing naturally abundant visible light will significantly impact this field.[34]

2) PCP derivatives have been promising platforms to study the element of planar chirality.[35] Regioselective functionalization and chiral resolution strategies give access to PCPs with planar and central chirality.[36] Another aspect of cyclophanyl-derived ligand design is the ability to incorporate planar chirality. Incorporating the element of chirality and preparing enantiomerically pure planar and central chiral cyclophanyl multimetallic complexes with M-to-M distance modulation would be beneficial, especially for later use in asymmetric transformations and promising precursor components in chiroptical material applications.

3) Along with synthetic progress, in silico calculations of structures and properties of metal complexes have shown tremendous progress.[37] For higher accuracy, combining computation of cyclophanes with experiments has become an established powerful tool.[38] Hence, structural optimization aided by advanced computational studies would be beneficial for screening large sets of ligands and fundamental understanding of complexes' electronic structure and properties. 4) Beyond developing synthetic methods for various metal complexes, capitalizing on collaborative research efforts combining theoretical modeling, design/synthesis, characterization/spectroscopy, and exploring catalytic, magnetic, and optical properties of novel organometallic complexes would be rewarding in countless ways for fundamental and practical explorations (Figure 6). This would aid in preparing efficient organometallic complexes.

3. Summary and Outlook

We would like to summarize some points: 1) The field of organometallic and coordination chemistry, each involving complexes of transition or lanthanide metals, is rapidly evolving from fundamental curiosity to practical applications in catalysis, optoelectronics, and other materials. While some of the fundamental relationships connecting metal center interactions and the resulting molecular properties are gradually coming into focus, many questions remain unanswered. Exploring innovative ligands can open new ways. Synthesis of model homo- and heterometallic cyclophanyl complexes with varying M-to-M distances by using differently functionalized PCP regioisomers including pseudo-*para*, -*ortho*, -*meta*, and -*gem*, derivatives have been realized. Small variations in a PCP ligand structure can cause changes in the sterics, and electronics have a prominent influence on chemical reactivity. As in an initial

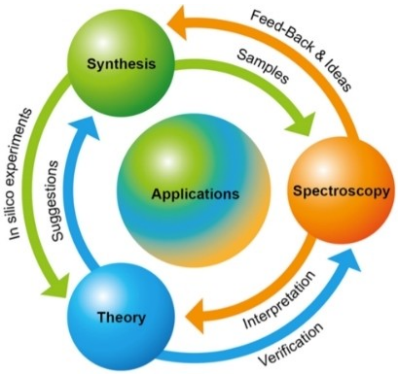

Figure 6. Cooperative research efforts by theoretical modeling, design/synthesis, and characterization of organometallic complexes (reproduced from SFB/TRR 88 resources; Copyright 2018 3MET). .

For further diversification studies, methods of ultrafast time-resolved laser spectroscopy in condensed and gas-phase investigation of the dynamics and intermetallic cooperativity of photophysical, photochemical, and transport processes in transition metal-ligand systems could unveil more insights.[39] This could provide exciting new findings of complexes about the charge, spin, and energy, essential for controlling specific structural, photochromic, luminescence, or photoreactive (catalytic) properties. Our ongoing efforts aim to rationally tailor and explore the influence and/or limits of cyclophane-derived metallic complexes in catalysis as well as materials design.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cyclophanyl Complexes · ligand Design · M-to-M distancemodulation · structure-property correlation · [2.2] paracyclophane

[1] J. Campos, *Nat. Chem. Rev.* **2020**, *4*, 696–702.
[2] P. Buchwalter, J. Rosé, P. Braunstein, *Chem. Rev.* **2015**, *115*, 28–126.
[3] T. Klabunde, C. Eicken, B. Krebs, *Nat. Struct. Biol.* **1998**, *5*, 1084–1090.
[4] M. O. Ross, A. C. Rosenzweig, *J. Biol. Inorg. Chem.* **2017**, *22*, 307–319.
[5] Z. F. Kanyo, L. R. Scolnick, D. E. Ash, D. W. Christianson, *Nature* **1996**, *383*, 554–557.
[6] N. Strater, T. Klabunde, P. Tucker, H. Witzel, B. Krebs, *Science* **1995**, *268*, 1489–1492.
[7] H. Dobbek, V. Svetlitchnyi, L. Gremer, R. Huber, O. Meyer, *Science* **2001**, *293*, 1281–1285.
[8] R. Peters, Cooperative Catalysis: Designing Efficient Catalysts for Synthesis, Wiley-VCH, Weinheim, **2015**.
[9] R. Maity, B. S. Birenheide, F. Breher, B. Sarkar, *ChemCatChem* **2021**, *13*, 2337–237.
[10] a) J. A. Mata, F. E. Hahn, E. Peris, *Chem. Sci.* **2014**, *5*, 1723–1732; b) J. Park, S. Hong, *Chem. Soc. Rev.* **2012**, *41*, 6931–6943.
[11] a) S. Martínez, L. Veth, B. Lainer, P. Dydio, *ACS Catal.* **2021**, *11*, 3891–3915; b) I. Bratko, M. Gomez, *Dalton Trans.* **2013**, *42*, 10664–10681.
[12] a) I. G. Powers, C. Uyeda, *ACS Catal.* **2017**, *7*, 936–958; b) C. Schissler, E. K. Schneider, B. Felker, P. Weis, M. Nieger, M. M. Kappes, S. Bräse, *Chem. Eur. J.* **2021**, *27*, 3047–3054.
[13] a) A. N. Desnoyer, A. Nicolay, P. Rios, M. S. Ziegler, T. D. Tilley, *Acc. Chem. Res.* **2020**, *53*, 1944–1956; b) R. H. D. Lyngdoh, H. F. Schaefer III, R. B. King, *Chem. Rev.* **2018**, *118*, 11626–11706; c) M. D. Fryzuk, *Inorg. Chem.* **2015**, *54*, 9671–9674; d) P. J. Steel, *Acc. Chem. Res.* **2005**, *38*, 243–250.
[14] E. K. van den Beuken, B. L. Feringa, *Tetrahedron* **1998**, *54*, 12985–13011.
[15] Z. Hassan, E. Spuling, D. M. Knoll, J. Lahann, S. Bräse, *Chem. Soc. Rev.* **2018**, *47*, 6947–6963.
[16] a) C. Zippel, Z. Hassan, M. Nieger, S. Bräse, *Adv. Synth. Catal.* **2020**, *362*, 3431–3436; b) M. A. Petrukhina, A. S. Filatov, Y. Sevryugina, K. W. Andreini, S. Takamizawa, *Organometallics* **2006**, *25*, 2135–2142.
[17] a) D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1971**, *4*, 204–213; ; b) A. de Meijere, B. König, *Synlett* **1997**, 1221–1232; c) For a special Issue on Cyclophanes Chemistry: [2.2]Paracyclophane — After 60 Years, Stronger Than Ever, *Isr. J. Chem.* **2012**, *52*, 1–192; d) *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**.
[18] a) C. Bolm, K. Wenz, G. Raabe, *J. Organomet. Chem.* **2002**, *662*, 23–33; b) V. V. Dunina, E. I. Turubanova, M. V. Livantsov, K. A. Lyssenko, N. V. Vorontsova, D. Y. Antonov, Y. K. Grishin, *Tetrahedron: Asymmetry* **2009**, *20*, 1661–1671; c) J. E. Glover, P. G. Plieger, G. J. Rowlands, *Aust. J. Chem.* **2014**, *67*, 374–380; d) T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, S. Ogoshi, H. Kurosawa, *Angew. Chem. Int. Ed.* **2007**, *46*, 5440–5443; *Angew. Chem.* **2007**, *119*, 5536–5539; e) C. Zippel, T. Bartholomeyzik, C. Friedmann, M. Nieger, Z. Hassan, S. Bräse, *Eur. J. Org. Chem.* **2021**, 5090–5093.
[19] a) Z. Hassan, E. Spuling, D. M. Knoll, S. Bräse, *Angew. Chem. Int. Ed.* **2020**, *59*, 2156–2170; *Angew. Chem.* **2020**, *132*, 2176–2190; b) O. R. P. David, *Tetrahedron* **2012**, *68*, 8977–8993; c) S. E. Gibson, J. D. Knight, *Org. Biomol. Chem.* **2003**, *1*, 1256–1269.
[20] a) P. Mückea, M. Zabel, R. Edge, D. Collison, S. Clémentd, S. Záliše, R. F. Winter, *J. Organomet. Chem.* **2011**, *20*, 3186–3197; b) P. Mücke, R. F. Winter, K. Kowalski, *J. Organomet. Chem.* **2013**, *735*, 10–14; c) P. Mücke, R. F. Winter, I. Novak, K. Kowalski, *J. Organomet. Chem.* **2012**, *717*, 14–22; d) P. J. Ball, T. R. Shtoyko, J. A. K. Bauer, W. J. Oldham, W. B. Connick, *Inorg. Chem.* **2004**, *43*, 622–632.
[21] S. Clément, T. Goudreault, D. Bellows, D. Fortin, L. Guyard, M. Knorr, P. D. Harvey, *Chem. Commun.* **2012**, *48*, 8640–8642.
[22] a) M. Wielopolski, A. M. Ontoria, C. Schubert, J. T. Margraf, E. Krokos, J. Kirschner, A. Gouloumis, T. Clark, D. M. Guldi, N. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 10372–10381; b) A. M. Ontoria, M. Wielopolski, J. Gebhardt, A. Gouloumis, T. Clark, D. M. Guldi, N. Martin, *J. Am. Chem. Soc.* **2011**, *133*, 2370–2378.
[23] a) G. C. Bazan, *J. Org. Chem.* **2007**, *72*, 8615–8635; b) G. P. Bartholomew, G. C. Bazan, *Acc. Chem. Res.* **2001**, *34*, 30–39.
[24] a) S. Bräse, Planar Chiral Ligands based on [2.2]Paracyclophanes. Asymmetric Synthesis: The Essentials (Eds: M. Christmann, S. Bräse), Wiley-VCH, Weinheim, **2006**; b) S. Bräse, Asymmetric 1,2- Addition Reactions by Planar and Central Chiral [2.2]Paracyclophanes. *Asymmetric Synthesis with Chemical and Biological Methods*; D. Enders, Ed.; Wiley-VCH: Weinheim, **2007**; c) G. J. Rowlands, *Org. Biomol. Chem.* **2008**, *6*, 1527–1534; d) J. Paradies, *Synthesis* **2011**, 3749–3766.
[25] a) C. Sarcher, A. Lühl, F. C. Falk, S. Lebedkin, M. Kühn, C. Wang, J. Paradies, M. M. Kappes, W. Klopper, P. W. Roesky, *Eur. J. Inorg. Chem.* **2012**, 5033–5042; b) F. C. Falk, R. Fröhlich, J. Paradies, *Chem. Commun.* **2011**, *47*, 11095–11097; c) R J. Felix, D. Weber, O. Gutierrez, D. J. Tantillo, M. R. Gagne, *Nat. Chem.* **2012**, 405–409.
[26] a) D. M. Knoll, C. Zippel, Z. Hassan, M. Nieger, P. Weis, M. M. Kappes, S. Bräse, *Dalton Trans.* **2019**, *48*, 17704–17708; b) C. Zippel, R. Israil, L. Schüssler, Z. Hassan, E. Schneider, P. Weis, M. Nieger, C. Bizzarri, M. M. Kappes, C. Riehn, R. Diller, S. Bräse, "unpublished work".
[27] C. Braun, M. Nieger, W. R. Thiel, S. Bräse, *Chem. Eur. J.* **2017**, *23*, 15474–15483.
[28] a) C. Braun, E. Spuling, N. B. Heine, M. Cakici, M. Nieger, S. Bräse, *Adv. Synth. Catal.* **2016**, *358*, 1664–1670; b) S. Kitagaki, S. Murata, K. Asaoka, K. Sugisaka, C. Mukai, N. Takenaga, K. Yoshida, *Chem. Pharm. Bull.* **2018**, *66*, 1006–1014; c) D. M. Knoll, H. Simek, Z. Hassan, S. Bräse, *Eur. J. Org. Chem.* **2019**, *36*, 6198–6202; d) D. M. Knoll, Y. Hu, Z. Hassan, M. Nieger, S. Bräse, *Molecules* **2019**, *24*, 4122–4134; e) E. Polat, O. Turbedaroglu, M. Cakici, *Tetrahedron Lett.* **2021**, *67*, 152871–52872; f) M. N. Mungalpara, P. G. Plieger, G. J. Rowlands, *Adv. Synth. Catal.* **2021**, *363*, 1069–1080.

[29] D. M. Knoll, T. B. Wiesner, S. M. Marschner, Z. Hassan, P. Weis, M. Kappes, M. Niegerc, S. Bräse, *RSC Adv.* **2019**, *9*, 30541–30544.
[30] a) X. Wang, X. You, Z. P. Shang, J. Xia, *J. Organomet. Chem.* **2016**, *803*, 111–118; b) J. Xia, Y. P. Ou, D. Wu, G. J. Jin, J. Yin, G. A. Yu, S. H. Liu, *Dalton Trans.* **2013**, *42*, 14212–14222; c) J. L. Xia, W. Y. Man, X. Zhu, C. Zhang, G. J. Jin, P. A. Schauer, M. A. Fox, J. Yin, G. A. Yu, P. J. Low, S. H. Liu, *Organometallics* **2012**, *31*, 5321–5333.
[31] a) M. Gon, Y. Morisaki, Y. Chujo, *Chem. Commun.* **2017**, *53*, 8304–8307; b) J. Anhäuser, R. Puttreddy, Y. Lorenz, A. Schneider, M. Engeser, K. Rissanen, A. Lützen, *Org. Chem. Front.* **2019**, *6*, 1226–1235; c) J. Anhäuser, R. Puttreddy, L. Glanz, A. Schneider, M. Engeser, K. Rissanen, A. Lützen, *Chem. Eur. J.* **2019**, *25*, 12294–12297; d) D. R. Martir, L. Delforce, D. B. Cordes, A. M. Z. Slawin, S. L. Warriner, D. Jacquemin, E. Zysman-Colman, *Inorg. Chem. Front.* **2020**, *7*, 232–238.
[32] C. F. R. Mackenzie, L. Delforce, D. R. Martir, D. B. Cordes, A. M. Z. Slawin, E. Zysman-Colman, *Front. Chem.* **2021**, DOI: 10.3389/fchem.2021.728845.
[33] a) X. Xue, J. Wang, Q. Zhu, Y. Xuea, H. Liu, *Dalton Trans.* **2021**, *50*, 1374–1383; b) M. Cakici, Z. G. Gu, M. Nieger, J. Bürck, L. Heinke, S. Bräse, *Chem. Commun.* **2015**, *51*, 4796–4798; c) G. S. Papaefstathiou, T. Friščić, L. R. MacGillivray, *J. Am. Chem. Soc.* **2005**, *127*, 14160–14161.
[34] a) C. Stephenson, T. Yoon, *Acc. Chem. Res.* **2016**, *49*, 2059–2060; b) M. Kozlowski, T. Yoon, *J. Org. Chem.* **2016**, *81*, 6895–6897; c) M. H. Shaw, J. Twilton, D. W. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926; d) L. Marzo, S. K. Pagire, O. Reiser, B. Konig, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034–10072.
[35] a) S. Felder, S. Wu, J. Brom, L. Micouin, E. Benedetti, *Chirality* **2021**, *33*, 506–527; b) S. Fujita, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1515–1529; c) G. J. Rowlands, *Isr. J. Chem.* **2012**, *52*, 60–75; d) S. Bräse, S. Dahmen, S. Höfener, F. Lauterwasser, M. Kreis, R. E. Ziegert, *Synlett* **2004**, 2647–2669.
[36] C. Zippel, Z. Hassan, A. Q. Parsa, J. Hohmann, S. Bräse, *Adv. Synth. Catal.* **2021**, *363*, 2861–2865.
[37] a) S. H. Schiffer, *Acc. Chem. Res.* **2017**, *50*, 561–566.
[38] a) S. Grimme, C. M. Lichtenfeld, *Isr. J. Chem.* **2012**, *52*, 180–192; b) G. F. Caramori, S. E. Galembeck, *J. Phys. Chem. A* **2008**, *112*, 11784–11800; c) S. Grimme, *Chem. Eur. J.* **2004**, *10*, 3423–3429.
[39] a) M. Grupe, F. Bäppler, M. Theiß, J. M. Busch, F. Dietrich, D. Volz, M. Gerhards, S. Bräse, R. Diller, *Phys. Chem. Chem. Phys.* **2020**, *22*, 14187–14200; b) F. Bäppler, M. Zimmer, F. Dietrich, M. Grupe, M. Wallesch, D. Volz, S. Bräse, M. Gerhards, R. Diller *Phys. Chem. Chem. Phys.* **2017**, *19*, 29438–29448.

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