DOI: 10.1002/anie.201105940

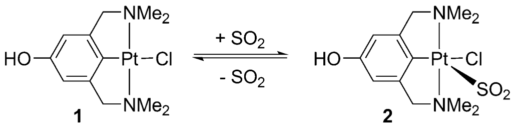
Consecutive Molecular Crystalline-State Reactions with Metal Complexes**

*Milko E. van der Boom**

catalysis · coordination chemistry ·
crystal engineering · transition metals

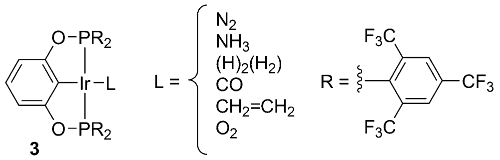
Crystal engineering is a rapidly developing field and many intriguing transformations have been demonstrated recently with molecular single crystals (SCs) without loss of their crystallinity.[1] Molecular SC–SC transformations that involve light-induced coupling of unsaturated hydrocarbons and host–guest interactions with molecular SCs are among the most studied systems.[2–7] For example, molecular SCs of "donut-shaped" metal–organic complexes undergo significant reversible conformation changes by uptake and release of solvents.[7] These and many other findings show that molecular SCs can undergo complex transformations including selective chemical reactions without degradation of the ordered assembly; hence, many exciting possibilities lie ahead. Molecular SC–SC transformations have been envisioned to be used for metal-mediated reactions, catalysis, storage, separation, and sensing. Importantly, the formation of these functional materials requires reversible and/or stepwise internal SC–SC transformations involving organic substrates, reagents, and/or various analytes. However, only a limited number of examples regarding ligand-exchange reactions within molecular SCs of metal complexes has been reported during the last decade.[8–14] Reactions with SCs are commonly accompanied by the loss of single crystallinity, but the highlighted examples that follow show that (reversible) chemical reactions and even selective catalysis can occur within molecular SCs of diverse late-transition metal complexes.

In 2000, van Koten and co-workers demonstrated the adsorption of SO_2 by molecular SCs consisting of platinum pincer complexes (Scheme 1). Complex **1** forms a supramolecular network in the solid state induced by Pt−Cl···H−O interactions. Exposing the crystals of complex **1** to gaseous SO_2 results in the formation of an adduct (**2**). This SC–SC transformation is accompanied by significant changes in the geometry around the d^8 metal center from a square-planar (**1**) to an approximately square-pyramidal structure (**2**). Release of SO_2 afforded again complex **1** as a crystalline powder.



Scheme 1. Reversible adsorption of SO_2 by platinum pincer complexes.[8,9]

SCs of iridium pincer complex **3**, shown in Scheme 2, undergo a series of metal–ligand exchange processes with a variety of gaseous compounds (e.g., N_2, NH_3, H_2, CO, C_2H_4, and O_2).[11] Selective hydrogenation of ethylene in the presence of propylene was also observed when reactive surface sites were blocked with CO. Regarding these remarkable SC–SC transformations, Brookhart and co-workers showed that SCs of complex **3** serve as reactor vessels;[11] at the same time, they provide an efficient barrier by preventing the larger olefin from reaching the catalyst. SC-induced selectivity was reported earlier by Supriya and Das.[13] They observed that coordinated water of an iron cluster can be selectively and reversibly exchanged for methanol in the presence of different alcohols.



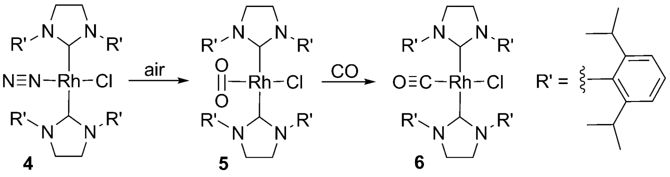
Scheme 2. Iridium pincer complexes that can undergo a series of reversible SC–SC transformations by ligand (L) exchange (irreversible for the CO ligand). SCs of complex **3** are also selective olefin-hydrogenation catalysts.[11]

In one of the latest examples of molecular SC–SC transformations, Crudden and co-workers reported a stepwise reaction with rhodium–N-heterocyclic carbene (NHC) complexes and gaseous compounds (Scheme 3).[12] The η^1-coordinated N_2 ligand of complex **4** is substituted by O_2 (in air) to afford complex **5**. Subsequently, the side-on bound O_2 ligand

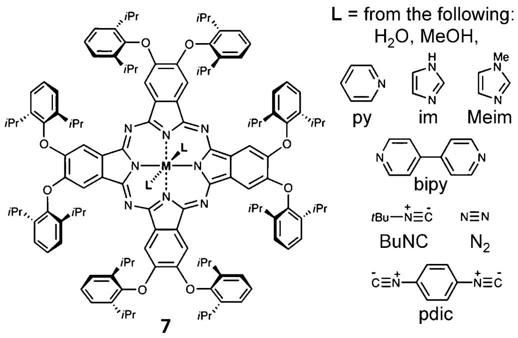
---

[*] Prof. M. E. van der Boom
Department of Organic Chemistry
The Weizmann Institute of Science, Rehovot, 76100 (Israel)
E-mail: milko.vanderboom@weizmann.ac.il
Homepage: https://sites.google.com/site/milkovanderboomslab/

[**] This research was supported by the Helen and Martin Kimmel Center for Molecular Design. M.B. is the incumbent of the Bruce A. Pearlman Professorial Chair in Synthetic Organic Chemistry.



Scheme 3. Rhodium-N-heterocyclic carbene (NHC) complexes with bulky substituents reacting with O_2 and CO.[12]



Scheme 4. Nanoporous molecular crystals of an iron phthalocyanine derivative (**7**) undergo axial ligand (L) exchange with the listed compounds from solution or the gas-phase.[10]

is readily irreversibly replaced by η^1-coordinated CO upon exposure of the crystals of complex **5** to a CO atmosphere. These molecular SC conversions occur with no fracturing of individual crystals, and are accompanied by significant color changes observable by naked eye (**4**: yellow, **5**: blue, **6**: brown). The bulky substituents of the NHC ligand might prevent the oxidation of the low-valent rhodium centers ($\mathbf{4} + O_2 \rightarrow \mathbf{5} + N_2$).

Ligand-exchange reactions with late-transition metals have been thoroughly studied in solution.[15] To date, little is known regarding the mechanism underlying such processes with SCs. N_2 remains bound to rhodium upon days of exposing crystals of complex **4** to argon or vacuum;[12] Brookhart also reported that the iridium complex **3**-N_2 is stable under vacuum.[11] These observations indicate that the ligand exchange takes place within these SCs. However, complex **2** releases SO_2 gas upon exposure to an inert atmosphere.[8,9] Apparently, dissociative processes might also occur, depending on the nature of the metal complex used. The ligand-exchange reactions are likely to be complex because the crystal surface and the packing of the complexes are additional parameters that might play dominant roles. Absorption and desorption of gaseous molecules on the large surface of a crystalline material is probably fast in comparison with the transport and metal–ligand exchange reactions that occur within the SCs. These processes might be accompanied by reorganization of the supramolecular structure as observed by van Koten.[8,9] However, the Brookhart[11] and Crudden[12] SC–SC transformations do not change the space groups and hardly affect the lattice parameters. The reaction time might be dependent on crystal-size.

The abovementioned examples are characterized by ligand exchange with small gaseous molecules (Scheme 1–3).[8,9,11,12] The scope of SC transformations with ligands of well-defined metal complexes is not limited to organometallic compounds and solid state–gas phase reactions. Iron phthalocyanine molecular SCs rapidly exchange axial ligands with organic compounds from solution and from the gas phase (Scheme 4).[10] The solid-state assembly of complex **7** consists of millimeter-size crystals having large 8 nm^3 voids and interconnecting channels. Therefore, this heme model system can undergo exchange reactions with monodentate ligands (e.g., BuNC, pyridine, *N*-methylimidazole) or with bidentate ligands that can even bridge between two metal centers. For example, 4,4′-bipyridyl (bipy) and 1,4-phenylenediisocyanide (pdic) have the proper length (ca. 1 nm) to bind simultaneously to the metal centers of two phthalocyanines.

Reactions with molecular SCs of organometallic and coordination complexes are still rare. Pincer,[16,17] NHC,[18] and phthalocyanine-type[19] complexes catalyze a wide range of chemical reactions in solution. Reactions catalyzed by metal complexes in the confined space offered by the SCs might lead to products that are not readily attainable otherwise.[20] The remarkable findings from McKeown and co-workers regarding the nanoporous single crystals of an iron phthalocyanine derivative (**7**; Scheme 4) suggest that it should be possible to functionalize organic substrates from solution within the solid-state assembly followed by product release.[10] In this respect, SCs of rhenium dinitrosyl complexes undergo oxidation of one of the nitrosyl ligands while retaining crystallinity.[21] To achieve rational design of functionality and new SC reactions, more fundamental studies are needed to gain detailed mechanistic insight. This research should include designing nanoporous molecular SCs of reactive metal complexes that retain their monocrystallinity during chemical reactions. The molecular crystalline assembly should not be affected by (minor) structural changes or should adapt to new situations and working environments with ease.[6] Whether molecular SC transformations, such as the highlighted examples cited here,[8–12] will provide materials with useful properties superior to other systems, such as metal-organic frameworks (MOFs),[22,23] is a challenging open question, which should be addressed in future research.

Received: August 23, 2011

---

[1] a) D. Braga, F. Grepioni, *Chem. Commun.* **2005**, 3635–3645; b) N. B. McKeown, *J. Mater. Chem.* **2010**, *20*, 10588–10597.

[2] For seminal examples: a) H. Nakanishi, W. Jones, J. M. Thomas, *Chem. Phys. Lett.* **1980**, *71*, 44–48; b) G. M. J. Schmidt, *J. Chem. Soc.* **1964**, 2014–2021.

[3] M. Nagarathinam, A. M. P. Peedikakkal, J. J. Vittal, *Chem. Commun.* **2008**, 5277–5288.

[4] L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, T. D. Hamilton, D. K. Bučar, Q. Chu, D. B. Varshney, I. G. Georgiev, *Acc. Chem. Res.* **2008**, *41*, 280–291.

[5] C. Massera, M. Melegari, E. Kalenius, F. Ugozzoli, E. Dalcanale, *Chem. Eur. J.* **2011**, *17*, 3064–3068.

[6] J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science* **2002**, *298*, 1000–1002.

[7] L. Dobrzańska, G. O. Lloyd, C. Esterhuysen, L. J. Barbour, *Angew. Chem.* **2006**, *118*, 5988 – 5991; *Angew. Chem. Int. Ed.* **2006**, *45*, 5856 – 5859.

[8] M. Albrecht, M. Lutz, A. L. Spek, G. van Koten, *Nature* **2000**, *406*, 970 – 974.

[9] M. Albrecht, M. Lutz, A. M. M. Schreurs, E. T. J. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2000**, 3797 – 3804.

[10] C. G. Bezzu, M. Helliwell, J. E. Warren, D. R. Allan, N. B. McKeown, *Science* **2010**, *327*, 1627 – 1630.

[11] Z. Huang, P. S. White, M. Brookhart, *Nature* **2010**, *465*, 598 – 601.

[12] O. V. Zenkina, E. C. Keske, R. Wang, C. M. Crudden, *Angew. Chem.* **2011**, *123*, 8250 – 8254; *Angew. Chem. Int. Ed.* **2011**, *50*, 8100 – 8104.

[13] S. Supriya, S. K. Das, *J. Am. Chem. Soc.* **2007**, *129*, 3464 – 3465.

[14] K. Uehara, N. Mizuno, *J. Am. Chem. Soc.* **2011**, *133*, 1622 – 1625.

[15] For an example, see: A. Vigalok, Y. Ben-David, D. Milstein, *Organometallics* **1996**, *15*, 1839 – 1844.

[16] M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866 – 3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750 – 3781.

[17] M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759 – 1792.

[18] S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612 – 3676.

[19] E. M. Sul'man, B. V. Romanovskii, *Russ. Chem. Rev.* **1996**, *65*, 609 – 616.

[20] Y. Inokuma, M. Kawano, M. Fujita, *Nat. Chem.* **2011**, *3*, 349 – 358.

[21] C. M. Frech, O. Blacque, H. W. Schmalle, H. Berke, *Dalton Trans.* **2006**, 4590 – 4598.

[22] D. Zacher, R. Schmid, C. Wöll, R. A. Fischer, *Angew. Chem.* **2011**, *123*, 184 – 208; *Angew. Chem. Int. Ed.* **2011**, *50*, 176 – 199.

[23] D. Zhao, D. J. Timmons, D. Yuan, H.-C. Zhou, *Acc. Chem. Res.* **2011**, *44*, 123 – 133.