however, it is conceivable that other trivalent ions, such as Al^{3+}, B^{3+}, and Cr^{3+}, may pair with Fe^{3+} and substitute for the Mg^{2+}-Si^{4+} pair, thus favoring the formation of Fe^{3+} by oxidizing Fe^{2+}. This paired substitution provides an interpretation for the reported increase of the apparent K values in the presence of Al_2O_3 (*21*), B_2O_3 (*23*), and a variety of transition-element oxides (such as Ni, Cr, and Mn) (*16*). Major and trace element partitioning could thus be coupled with ferrous and ferric distributions. The electrical conductivity (*8*, *10*, *38*), radiative heat transfer, and melting behavior (*9*) are all highly dependent on the Fe contents and oxidation states of component phases. Likewise, the density, thermal expansion, and elasticity of the mantle models (*4*, *7*, *39*, *40*) must be adjusted with variable composition.

REFERENCES AND NOTES

1. L. G. Liu, *Nature* **258**, 510 (1975).
2. E. Knittle and R. Jeanloz, *Science* **235**, 668 (1987).
3. D. L. Anderson, *ibid.* **243**, 367 (1989).
4. H. K. Mao *et al.*, *J. Geophys. Res.* **96**, 8069 (1991).
5. L. Stixrude, R. J. Hemley, Y. Fei, H. K. Mao, *Science* **257**, 1099 (1992).
6. R. Jeanloz, *Nature* **378**, 130 (1995).
7. A. Yeganeh-Haeri, D. J. Weidner, E. Ito, *Science* **243**, 787 (1989).
8. X. Li and R. Jeanloz, *J. Geophys. Res.* **96**, 6113 (1991).
9. A. Zerr and R. Boehler, *Science* **262**, 553 (1993).
10. J. P. Poirier, A. Goddat, J. Peyronneau, *Philos. Trans. R. Soc. London Ser. A* **354**, 1361 (1996).
11. J. Li and C. B. Agee, *Nature* **381**, 686 (1996).
12. V. J. Hillgren, M. J. Drake, D. C. Rubie, *Science* **264**, 1442 (1994).
13. E. Knittle and R. Jeanloz, *ibid.* **251**, 1438 (1991).
14. V. R. Murthy, *ibid.* **253**, 303 (1991).
15. J. H. Jones, C. J. Capobianco, M. J. Drake, *ibid.* **257**, 1281 (1992); V. R. Murthy, *ibid.*, p. 1284.
16. S. E. Kesson and J. D. FitzGerald, *Earth Planet. Sci. Lett.* **111**, 229 (1991).
17. Y. Fei, Y. Wang, L. W. Finger, *J. Geophys. Res.* **101**, 11 (1996).
18. T. Yagi, H. K. Mao, P. M. Bell, *Carnegie Inst. Washington Yearb.* **78**, 612 (1979).
19. F. Guyot, M. Madon, J. Peyronneau, J. P. Poirier, *Earth Planet. Sci. Lett.* **90**, 52 (1988).
20. E. Ito, E. Takahashi, Y. Matsui, *ibid.* **67**, 238 (1984).
21. B. J. Wood and D. C. Rubie, *Science* **273**, 1522 (1996).
22. C. McCammon, *Nature* **387**, 694 (1997).
23. T. Katsura and E. Ito, *Geophys. Res. Lett.* **23**, 2005 (1996).
24. I. Martinez, Y. Wang, F. Guyot, R. C. Liebermann, *J. Geophys. Res.* **102**, 5265 (1997).
25. With regard to oxidation, multianvil presses involve open systems in which the ferric/ferrous ratio is not controlled by the starting samples but varied by a buffering condition specific to the cell assemblage. These experiments demonstrated that adding Al_2O_3 would indirectly assist oxidizing Fe^{2+} to form Fe^{3+} in pv (*21*, *22*). The Al_2O_3 effect, therefore, is a Fe^{3+} effect.
26. G. Shen, H. K. Mao, R. J. Hemley, in *Advanced Materials '96—New Trends in High Pressure Research* (National Institute for Research on Inorganic Materials, Tsukuba, Japan, 1996), pp. 149–152.
27. Fo_{65} (A), Fo_{60} (C), and En_{60} (F) were synthesized by and courtesy of D. H. Lindsley of State University of New York, Stony Brook (letters in parenthesis indicate the batch numbers in Lindsley's system). Other samples were synthesized at the Geophysical Laboratory of the Carnegie Institution of Washington.
28. A. J. Campbell, D. L. Heinz, A. M. Davis, *Geophys. Res. Lett.* **19**, 1061 (1992).
29. H. K. Mao and R. J. Hemley, *High Pressure Res.* **14**, 257 (1996).
30. We used polychromatic x-radiation at the superconducting wiggler beam line (X17C) at the National Synchrontron Light Source (NSLS) and the bending magnet beam line (sector 13) at the Advanced Photon Source (APS) for energy dispersive x-ray diffraction (EDXD). With the high intensity of the synchrotron sources and Kirkpatrick-Baez focusing mirrors (*41*), the EDXD of the 5-μm spots yielded compositional precisions comparable with those of larger samples determined with conventional Debye-Scherrer film technique (*18*, *31*, *32*): ±0.03 for X_{Fe}^{pv} and ±0.02 for X_{Fe}^{mw}.
31. B. Simons, *Carnegie Inst. Washington Yearb.* **79**, 376 (1980).
32. Y. Fei, H. K. Mao, B. O. Mysen, *J. Geophys. Res.* **96**, 2157 (1991).
33. C. Meade, H. K. Mao, J. Hu, *Science* **268**, 1743 (1995).
34. S. K. Saxena *et al.*, *ibid.* **274**, 1357 (1996).
35. P. M. Bell, T. Yagi, H. K. Mao, *Carnegie Inst. Washington Yearb.* **78**, 618 (1979).
36. J. S. Olsen, C. S. G. Cousins, L. Gerward, H. Jhans, B. J. Sheldon, *Phys. Scr.* **43**, 327 (1991).
37. K. Weng, W. Gan, G. Wang, in *Developments in Geochemistry* (Seismological Press, Beijing, China, 1992), pp. 171–178.
38. X. Li, L. C. Ming, M. H. Manghnani, *J. Geophys. Res.* **98**, 501 (1993).
39. Y. Wang, D. J. Weidner, R. C. Liebermann, Y. Zhao, *Phys. Earth Planet. Inter.* **83**, 13 (1994).
40. T. Yagi and N. Funamori, *Philos. Trans. R. Soc. London Ser. A* **354**, 1371 (1996).
41. P. J. Eng, M. Rivers, B. X. Yang, W. Schildkamp, *Proc. Soc. Photo-Opt. Instrum. Eng.* **2516**, 41 (1996).
42. We thank D. H. Lindsley for providing the starting materials and NSLS and APS for providing the synchrotron beam. Supported by NSF grants from the Division of Earth Science and Center for High Pressure Research.

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Impact of Molecular Order in Langmuir-Blodgett Films on Catalysis

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Catalytically active Langmuir-Blodgett films of a rhodium complex were prepared and characterized to determine the possible effect of the molecular order of metal complexes on catalytic activity. The hydrogenation of carbon-oxygen double bonds was used as a model reaction. The complex in solution exhibited low catalytic activity, whereas it was highly active in the film. The catalytic activity was found to be highly dependent on the orientation of the complex within the film. The reactions were also highly selective with regard to the substrate. These observations and the observed rate dependence on temperature strongly implicate the molecular order of a metal complex as an important dimension in catalysis.

Homogeneous catalysis by metal complexes plays a major role in chemical and biological processes and is used for the production of millions of tons of chemicals annually (*1*). By controlling and modifying the properties of the metal center, the catalytic activity can be optimized and high degrees of efficiency and selectivity can be achieved. Such catalysis generally involves discrete metal complexes that function independently of each other. We are interested in the properties of highly ordered, two-dimensional structures with catalytically active metal complexes. Our approach is based on the generation of Langmuir-Blodgett (LB) films from appropriately modified complexes. This approach allows analysis of the films by well-established analytical methods (*2*). The catalytic activity of the film may be controlled by systematic structural modifications. Furthermore, synergistic effects may occur as a result of interactions of molecules in a close-packed LB film.

Recently, an approach to the generation of chemically bound layers of metal complexes, which exhibit catalytic activity quite similar to that of the complexes in solution, was reported (*3*). We report here on the generation of LB films of a rhodium complex, which show high catalytic activity, whereas the complex exhibits low activity in a homogeneous system. Moreover, the catalyst exhibits remarkably high substrate selectivity and is highly dependent on the order and orientation of the films. The importance of order in the layer is also clearly manifested in the observed dependence of the rate on temperature.

We chose to study the amphiphilic complex **1** (Scheme 1), an analog of the known air- and water-stable hydrogenation catalyst (bipy)rhodium(hexadiene)PF_6 (bipy = bipyridine) (*4*). This complex was prepared by reaction of the ligand 4,4′-diheptadecyl-2,2′-bipyridine (*5*) with [Rh(hexadiene)

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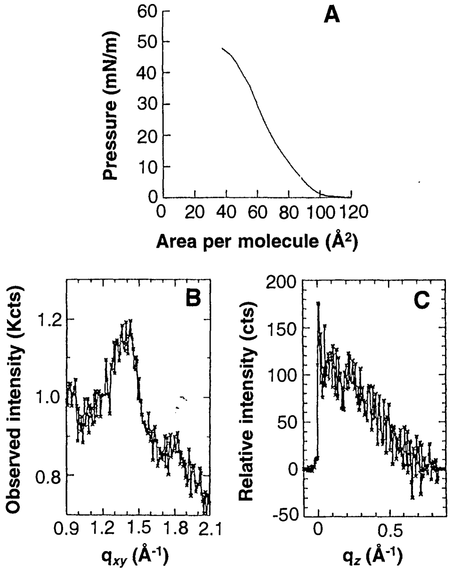


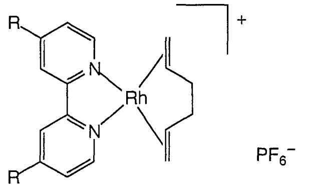
Fig. 1. (**A**) Pressure-area isotherm of complex **1** on water (compression rate: 20 mm/min, collapse point at 48 mN/m, area per molecule = 55 Å^2). (**B**) Bragg peak and (**C**) Bragg rod intensity profile obtained from complex **1** measured at 5°C and at 45 mN/m, by grazing incidence x-ray diffraction on water (cts, counts; Kcts, kilocounts, in arbitrary units; $\mathbf{q}_{xy}$ and $\mathbf{q}_z$ are the horizontal and vertical scattering vectors, respectively) (*16*).

Table 1. Hydrogenation of acetone to isopropanol for LB and solution systems. NR, no reaction. Reaction conditions: 72 psi H_2, 48 hours, 25°C, 0.11 mM acetone in water.

Glass type	Catalyst	Turnover
Hydrophilic	None	NR
Hydrophobic	None	NR
–	Suspension of complex **1**	NR
–	Complex **2**, saturated aqueous solution	NR
–	Solution, separated from monolayer after catalysis	No further reaction
Hydrophobic	Monolayer	60,000
Hydrophilic	Quadruple layer	70,000
Hydrophilic	Triple layer	NR
–	Monolayer on water surface	50,000
–	Monolayer on water surface, stirred	NR
–	Complexes **1** or **2** in neat acetone	500

Cl]$_2$ in methanol in analogy to a literature procedure (*4*), followed by precipitation of the complex by addition of NaPF$_6$.

Complex 1 forms a stable monolayer on the air-water interface (Fig. 1A). We transferred the monolayer from the water surface to hydrophilic or hydrophobic glass slides, at a pressure of 20 mN/m, using the Langmuir-Blodgett technique (*6*). The conformation-sensitive symmetric and asymmetric CH$_2$-stretching frequencies in the infrared (IR) spectrum of the compressed layer (on water and on gold-coated glass) indicate closely packed and ordered structures (*7*). The ultraviolet (UV) spectra of the complex in solution and of the transferred monolayer were the same, indicating that the complex maintained its structure.



1, R = $CH_3(CH_2)_{16}$
2, R = CH_3

Scheme 1. Catalytic rhodium complexes.

The degree of ordering in the monolayer was determined by synchrotron grazing incidence x-ray diffraction measurements performed on water at 5°C (Fig. 1B). A single Bragg diffraction peak at a q_{xy} = (4π/λ) sin(θ) value of 1.36 Å^{-1}, corresponding to a *d*-spacing of 4.6 Å, was obtained (where q_{xy} is the horizontal scattering vector, 2θ is the diffraction angle, and λ is the wavelength). The average crystallite size, as determined from the full width at half maximum (FWHM) of the Bragg peak, was ~45 Å, indicating a relatively low degree of order in the monolayer. The film thickness, as estimated from the FWHM of the Bragg rod intensity profile (Fig. 1C), was 21 Å, a value compatible with the length of the alkyl chains that mostly contributed to the diffraction.

The catalytic activity was studied with two types of LB films having opposite top layer orientations, tail-to-glass (monolayer on hydrophobic glass, hereafter denoted as ML, and quadruple layer on hydrophilic glass hereafter denoted as QL) and head-to-glass (triple layer on hydrophilic glass, hereafter denoted as TL) (Fig. 2). The supported LB films were tested as catalysts for the hydrogenation of acetone in a dilute aqueous solution (about 0.6% or 0.1 M) at room temperature under 72-psi hydrogen pressure without stirring (*8*). The transferred ML exhibited good catalytic activity [60,000 turnovers in 48 hours (*9*)], yielding isopropanol as the only observed product [as analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS)]. The QL showed a slightly higher activity (70,000 turnovers in 48 hours), perhaps as a result of the higher degree of order in the multilayer due to better smoothing of small defects on the glass surface.

Solutions of complexes 1 or 2 in neat acetone under similar reaction conditions showed much lower activity (500 turnovers in 48 hours). No reduction of acetone was observed with suspensions of complex 1 in water, showing that the monolayer is required for catalysis (*10*). Saturated aqueous solutions of the parent complex 2 also did not catalyze the reduction of acetone under the conditions used.

When the solution of a catalytic reaction was separated from the monolayer and allowed to react further, no additional acetone hydrogenation was observed, indicating that the reaction is not catalyzed by soluble structures that might have been formed (such as micelles or membranes). On the other hand, continuing the same reaction in the renewed presence of the monolayer resulted in further acetone hydrogenation.

One of the most revealing experiments was performed with a triple layer of complex 1 on hydrophilic glass. Here the upper layer was oriented as head-to-glass (Fig. 2). Reduction of acetone was not observed, indicating that this orientation blocks the catalytically active centers. Moreover, this experiment indicates that under the conditions used the triple layer does not open up. The tail-to-glass double layer that would remain if the top layer was peeled off is expected to catalyze the reaction.

To test whether the transfer of the films to a glass slide is essential, we prepared monolayers by dropping a solution of the catalyst in methylene chloride on the aqueous solution surface (a 100 mM solution of acetone in water was used). After evaporation of the methylene chloride, an intact monolayer was formed (*11*). The catalyst concentration needs to be calculated exactly to give a densely covered surface (*12*). However, because of the small amounts used, errors can be large and the turnover rates can differ significantly from one run to

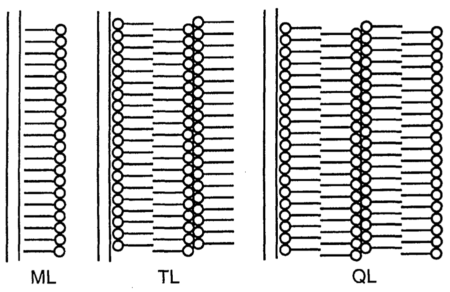


Fig. 2. Schematic presentation of the types of LB films used in this study: (left) ML on hydrophobic glass, (center) TL on hydrophilic glass, and (right) QL on hydrophilic glass.

Table 2. Hydrogenation of carbonyl compounds to alcohols. Reaction conditions: 72 psi H_2, 48 hours, 25°C, 0.11 mM carbonyl compound in water.

Glass type	Catalyst and substrate	Turnover number	Product
–	Complex **1** in neat acetone	500	Isopropanol
–	Complex **1** in neat acetone and butanone	500 (acetone), 300 (butanone)	Isopropanol + sec-butanol
Hydrophilic	QL, acetone and butanone	60,000 (acetone), NR (butanone)	Isopropanol
Hydrophilic	QL, butanone	NR	–
Hydrophilic	QL, acetaldehyde	40,000	Ethanol

another. Diluting the solution minimizes the error in volume but hinders good monolayer formation. Nevertheless, with this approach turnovers of around 50,000 (after 48 hours) were observed, showing that a monolayer on the air-water interface acts as an excellent catalyst as well. Significantly, no reaction was observed when the solution was stirred (Table 1).

The LB films have very high substrate selectivity (Table 2). When butanone was used instead of acetone, no product could be detected. Likewise, reaction of a 1:1 mixture of acetone and butanone showed high preference in favor of acetone (ratio of isopropanol to sec-butanol was greater than 100:1). In sharp contrast, both ketones were reduced without differentiation under homogeneous conditions in which a solution of complex **1** in a 1:1 mixture of the neat ketones was used, although low turnovers were obtained, as in the case of neat acetone (*13*). On the other hand, acetaldehyde was reduced by the quadruple layer to ethanol with about 40,000 turnovers in 48 hours, although other products were also formed (*14*).

It is known that monolayer crystallinity changes with temperature (*15*). Catalytic experiments at different temperatures using a quadruple layer are compatible with these changes (Fig. 3). At 4°C acetone was reduced with only a few turnovers. When the temperature was increased the rate increased as well, passing through a maximum at about 30°C and decreasing at higher temperatures. Importantly, the temperature effect was reversible; cooling the reaction from 45° to 30°C resulted in resumption of the high catalytic activity. In contrast, the hydrogenation activity of complex **1** in acetone solution, although relatively very low, exhibited the expected increase in catalytic activity with temperature (Fig. 3). We are unaware of such a temperature dependence for any other catalytic reaction.

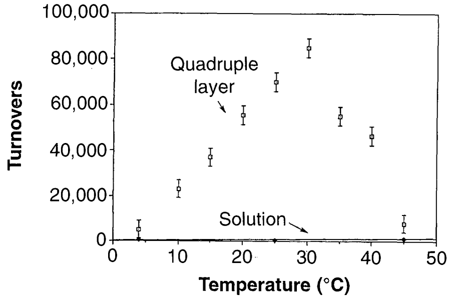


Fig. 3. Temperature effect on the hydrogenation of acetone (turnovers after 48 hours).

In contrast to acetone, the reduction of acetaldehyde with a quadruple layer, although not clean (*14*), occurred at 4°C with relatively high rates (34,000 turnovers in 48 hours). The rate increased with temperature and decreased above 30°C in this case as well.

These temperature effects suggest a major influence of LB film order on catalysis. The expected rate increase with temperature is observed as long as the ordered structure is maintained. At temperatures above 30°C the structure of the layer probably changes (from ordered to amorphous), resulting in the observed reactivity decrease. Upon cooling, the order is regenerated, with resumption of the catalytic activity.

We believe that these observations clearly demonstrate a major influence of ordered structures on a catalytic reaction. The catalytic activity of the rhodium complex **1** is dramatically increased in the ordered structure and it is highly dependent on layer orientation. Moreover, high substrate selectivity is observed, probably due to steric reasons. In addition, this reaction exhibits an unusual temperature effect in metal-complex catalysis, which can be explained by changes in molecular order in the layer. Further experiments are needed to gain mechanistic and structural understanding of these findings and extend them to other catalytic reactions.

REFERENCES AND NOTES

1. G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis* (Wiley, New York, ed. 2, 1992).
2. For an overview, see A. Ulman, *Thin Films, Organic Thin Films and Surfaces: Directions for the Nineties* (Academic Press, New York, 1995), vol. 20; and J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, *Comprehensive Supramolecular Chemistry Templating Self-Assembly and Self-Organisation* (Pergamon, New York, 1996), vol. 9.
3. M. G. L. Petrucci and A. K. Kakkar, *Adv. Mater.* **8**, 251 (1996); *J. Chem. Soc. Chem. Commun.* **1995**, 1577 (1995).
4. G. Mestroni, G. Zassimovich, A. Camus, *J. Organomet. Chem.* **140**, 63 (1977).
5. The ligand 4,4′-diheptadecyl-2,2′-bipyridine was prepared by double lithiation of 4,4′-dimethyl-2,2′-bipyridine, followed by reaction with 1-bromohexadecane [D. K. Ellison and R. T. Iwamato, *Tetrahedron Lett.* **24**, 31 (1983)].
6. The tail-to-glass oriented layers are stable only under water. When the slide is taken out through a compressed monolayer on the water surface, an additional layer is deposited, whereas without a monolayer (or with an uncompressed one) the transferred layer peels off. We solved this problem by handling the tail-to-glass loaded slides permanently under water. After the last layer transfer the slides were lowered into a prearranged vial, which served as the reaction container.
7. For the compressed monolayer on water, the CH_2-stretching frequencies are 2922.6 and 2853.9 cm^{-1}; for the quintuple layer on gold, the frequencies are 2925.0 and 2853.6 cm^{-1} [R. A. Deuhy and D. G. Cornell, in *Fourier Transform Spectroscopy in Colloid and Interface Science*, D. R. Scheiung, Ed. (ACS Symposium Series, Washington, DC, 1990), vol. 447, p. 192].
8. In a typical experiment, 50 mg of acetone was added to a vial containing 8 ml of double-distilled water (forming a 107.76 mM solution) and the layer-covered (~6 cm^2) glass slide. This vial was then transferred to a 90-ml Fisher-Porter type pressure flask. The flask was pressurized with 72 psi of hydrogen and allowed to react at room temperature for 48 hours without stirring. The solution was analyzed by GC and GC-MS.
9. Turnover numbers were calculated with the area per catalyst molecule (55 Å^2), the area on the slides covered with catalyst (measured for each transfer), and the amount of isopropanol formed (as detected by GC).
10. Complex **1** was inactive in both normal (hydrophilic) as well as hydrophobized reaction vessels. Hydrophobized reaction vessels were used to eliminate the possibility of the complex forming a head-to-glass layer on the walls of the vessel.
11. R. Popovitz-Biro *et al.*, *J. Am. Chem. Soc.* **116**, 1179 (1994).
12. Reactions with the monolayer directly on the water surface were carried out in hydrophobized Fisher-Porter pressure flasks (inner diameter, 2.6 cm; area, 5.3 cm^2; total volume, 35 ml) that were filled with 2 ml of a 100 mM aqueous acetone solution. The monolayer was spread on the water surface by applying with a syringe 2.6 μl from a 615 mM solution of complex **1** in methylene chloride. This amount was calculated to form a dense but uncompressed monolayer on the surface.
13. The turnover numbers after 48 hours (500 for acetone, 300 for butanone) are in accord with the different reactivity of the two ketones as reported in (*4*).
14. In addition to ethanol, the cyclic aldehyde trimer and acetic acid were also detected.
15. D. Jacquemain *et al.*, *Angew. Chem. Int. Ed. Engl.* **1**, 130 (1992), and references therein.
16. Note that the scattered intensity (counts) is measured over a range along the horizontal scattering vector $\mathbf{q}_{xy}$ but integrated over the whole position-sensitive detector (Psd) window. The Bragg rod shows the background-subtracted intensity along the vertical scattering vector $\mathbf{q}_z$ but integrated across the $\mathbf{q}_{xy}$ range of the Bragg peak. For further information, see J. Als-Nielsen *et al.*, *Phys. Rep.* **246**, 251 (1994).

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