



# Nanostructure Properties of Simple Organic and Organometallic Compounds



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## 1. Background

- Nanostructure synthesis by porous template wetting is well established [1]
- Template wetting typically used with polymer melts or multicomponent solutions [2]
- Hollis et al. used template wetting to make nanostructures from the di-Rh bis(N-heterocyclic) carbene in Figure 1 [3]

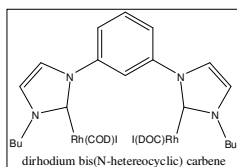


Figure 1 – Di-Rh NHC from Hollis et al.

- Nanostructures thought to be supported by Rh-Rh crosslinks
- What other features might allow for nanostructure formation?

## 2. Template Methodology

- Template is a 13 mm alumina disk with 0.02  $\mu\text{m}$  pores
- Compound of interest is dissolved in organic solvent
- Disk is saturated with solution and dried in air overnight
- Dry disk is dissolved in 3 N NaOH and solution is centrifuged
- Nanostructures appear as sediment in the centrifuge tube

## 3. Structural Factors

- 6 organometallic and 6 organic compounds were chosen
- Organometallic compounds chosen for variety among first row transition metals and presence of easily displaced ligands
- Organic compounds chosen for high molecular weight, potential for hydrogen bonding, and presence of nucleophilic and electrophilic sites in the same molecule

## 4. External Factors

- Structure is not the only factor in nanostructure formation
- Solvent polarity can affect the orientation of solute molecules
- Concentration affects the number of solute-solute interactions
- Three common organic solvents of increasing polarity were examined: toluene, methylene chloride, and acetonitrile
- Two concentrations studied:  $4.53 \times 10^{-5}$  M as in [3], and ten-fold higher  $4.53 \times 10^{-4}$  M

## 5. Compounds Investigated

- Organometallic compounds shown in Figure 2
- Organic compounds shown in Figure 3

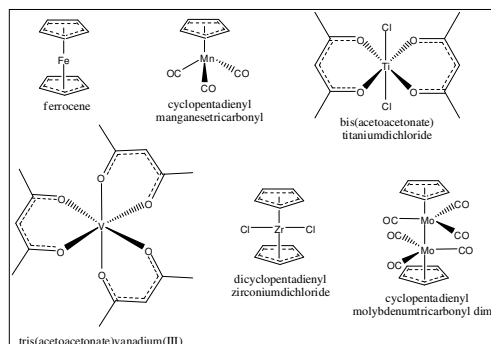


Figure 2 – Organometallic compounds

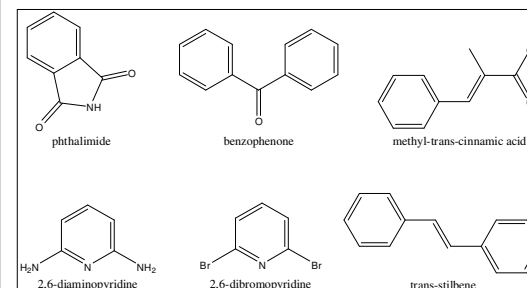


Figure 3 – Organic compounds

## 6. Results

- Solvent had no visible effect on nanostructure formation
- At original concentration, no compounds formed nanostructures
- At ten-fold concentration, bis(acetoacetonate) titanium dichloride formed a powdery white solid
- Based on facile oxidation of titanium chlorides and physical appearance of sample, the solid is likely composed of nanostructure  $\text{TiO}_2$

## 7. Conclusions

- Ability to form nanostructures governed primarily by structure and solution concentration
- Crosslinkable transition metal centers appear necessary for template nanostructure formation
- Potentially novel way to synthesize  $\text{TiO}_2$  nanostructures, which have useful catalytic properties [4]

## 8. Future Work

- Characterize suspected  $\text{TiO}_2$  samples by infrared spectroscopy and scanning electron microscopy
- Determine the nanostructure effects of small changes in the basic di-Rh NHC architecture
- Attempt nanostructure synthesis with NHC's incorporating other transition metals

## 9. References

- [1] M. Steinhart, J.H. Wendorff, A. Greiner, R.B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, & U. Gosele. *Science* 2002; 296: 1997
- [2] X. Zhang and S.K. Manohar. *J. Am. Chem. Soc.* 2005; 127: 14156
- [3] S. Ravindran, G.T.S. Andavan, C. Tsai, C.S. Ozkan, & T.K. Hollis. *Chem. Comm.* 2006; 1616-1618
- [4] S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, & L. Palmisano. *J. Am. Chem. Soc.* 2008; 130: 1568-1569