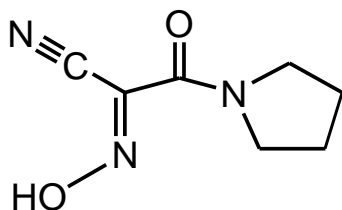


Ryan Kemp, 2011-2012

Ryan was enrolled in undergraduate research courses CHM 399 and CHM 499 and worked in my research laboratory for over a year. I invited him to try research in my group after his very good performance in my CHM 375 Inorganic Chemistry class in the Fall of 2010.

Ryan's project was totally new and exploratory! I assigned him to prepare new cyanoxime ligand of the amide type:



H(PyrCO), or 2-oximino-2-cyano-N-pyrrolidine acetamide

Thus, Ryan had to prepare target new cyanoxime using two steps procedure explained in Figure 1. After successful syntheses he grew crystals of both substituted N-pyrrolidine acetonitrile **I**, and then the cyanoxime **II**.

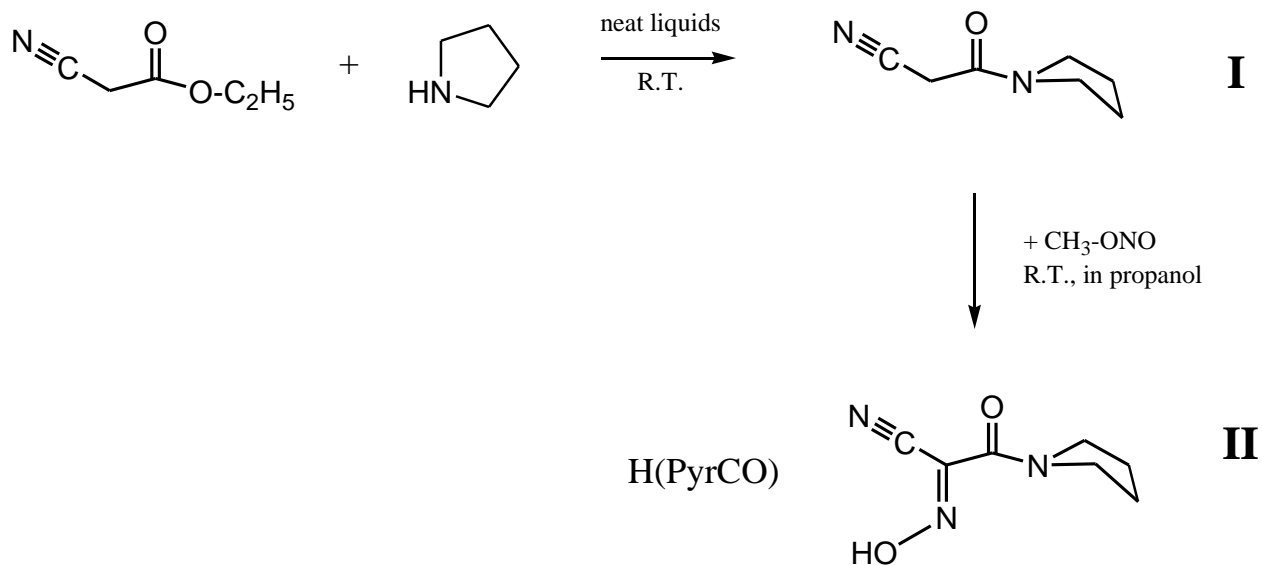


Figure 1. Developed synthetic route to a new cyanoxime ligand for inorganic chemistry.

Crystal structures of both compounds were determined and shown below in Figures 2 and Figure 3. It should be noted that the structure of the cyanoxime **II** is rather unique since in the asymmetric unit (ASU) there are 16 (!) independent molecules that form 8 H-bonded pairs (Figure 3).

When preparation of this new cyanoxime H(PyrCO) was fully developed, Ryan was asked to proceed with the new set of reactions to make more water soluble cyanoxime **IV** (Figure 4) from respective substituted acetonitrile-amide **III**. He successfully made that precursor, grew up suitable for the X-ray analysis crystals, and I have determined its crystal structure. It is shown in Figure 5. However, using gaseous methyl nitrite $\text{CH}_3\text{-ONO}$ in attempt to prepare desired cyanoxime **IV** did not lead to that product. Instead, cleavage of the entire N-piperazine fragment occurred and cyanoxime-carboxylic acid NC-C(=NOH)-COOH [abbreviated as H(AACO)] was formed.

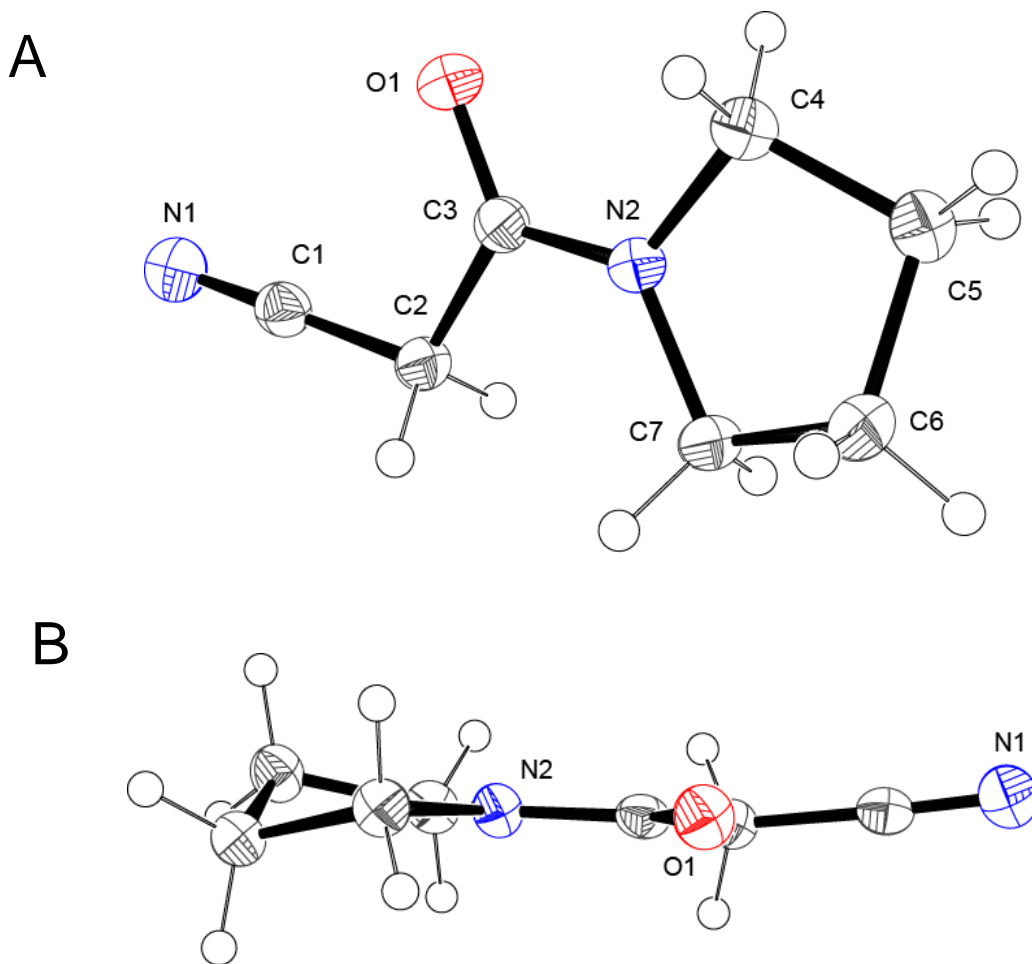


Figure 2. Molecular structure and numbering scheme for the N-pyrrolidine-cyanacetamide. An ORTEP drawing at 50% thermal ellipsoids probability level (A), and side view (B) of the molecule showing severe puckering of the pyrrolidine ring in the structure which leads to non-equivalence of all signals in the ^{13}C NMR spectrum of this compound.

Crystal data: T=120 K; in $P2_12_12_1$; R1 = 4.0%; GOF = 1.129.

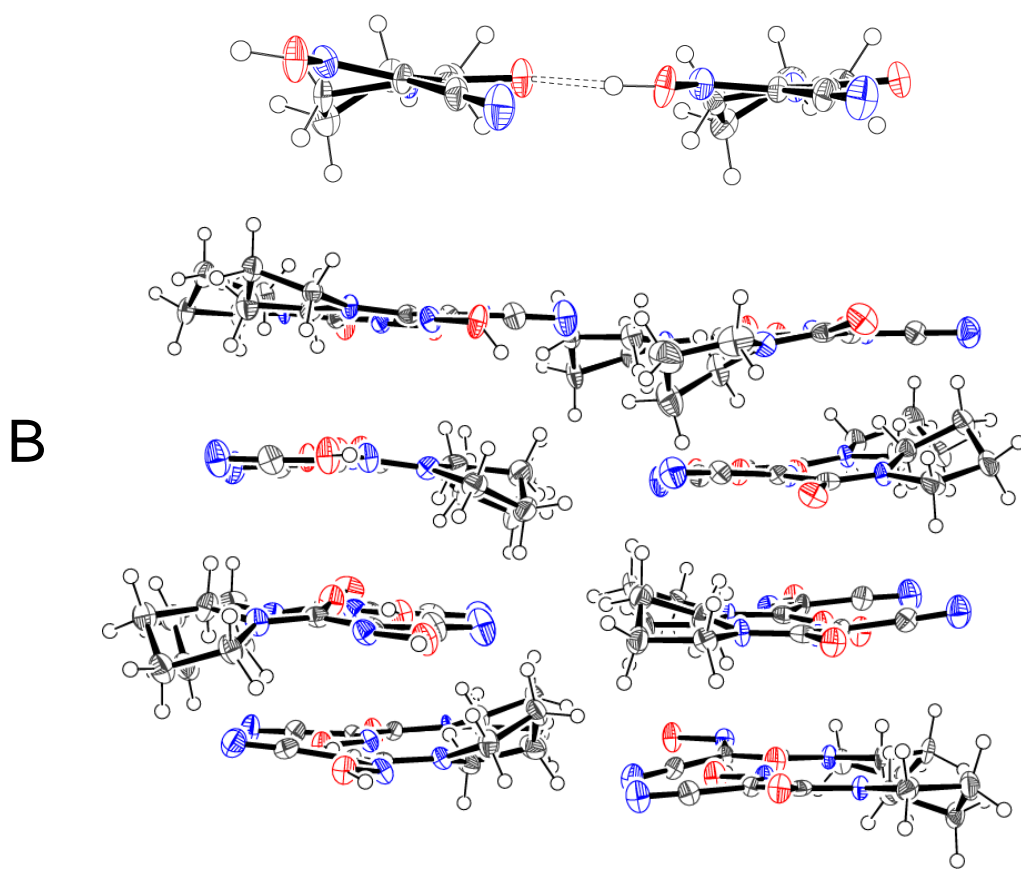
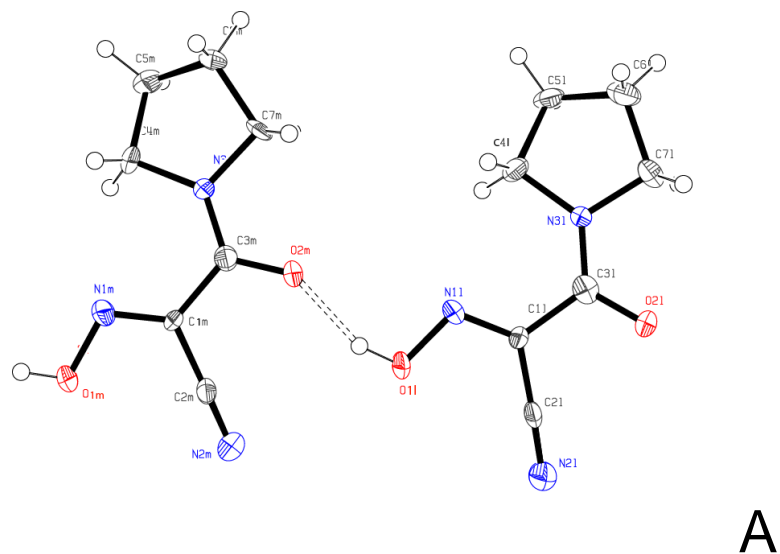


Figure 3. Molecular structure and numbering scheme for the 2-cyano-2-oximino-N-pyrrolidine-acetamide – two orthogonal views of one H-bonded pair (A), and the unit cell content showing 16 (!) independent H(PyrCO) molecules in the unit cell (B).

Crystal data: T=120 K; in P-1; R1 = 7.5%; GOF = 1.128.

What is remarkable to note is that both substituted acetonitrile precursors **I** and **III** crystal lattices are lacking the center of symmetry! Thus, **I** crystallizes in chiral orthorhombic space group $P2_12_12_1$, while the amide **III** crystallizes in $Pca2_1$ non-centrosymmetric space group. Both these compounds are new and never were obtained and studied before, and further investigation of their non-linear optical effect (NLO) as second harmonic generation is very much warranted.

After preparation and spectroscopic characterization of the H(PyrCO), it was time to make bivalent Pd and Pt complexes based on this cyanoxime. It was accomplished using simple two steps procedure shown in Figure 6 with actual complexes' appearance seen in Figure 7.

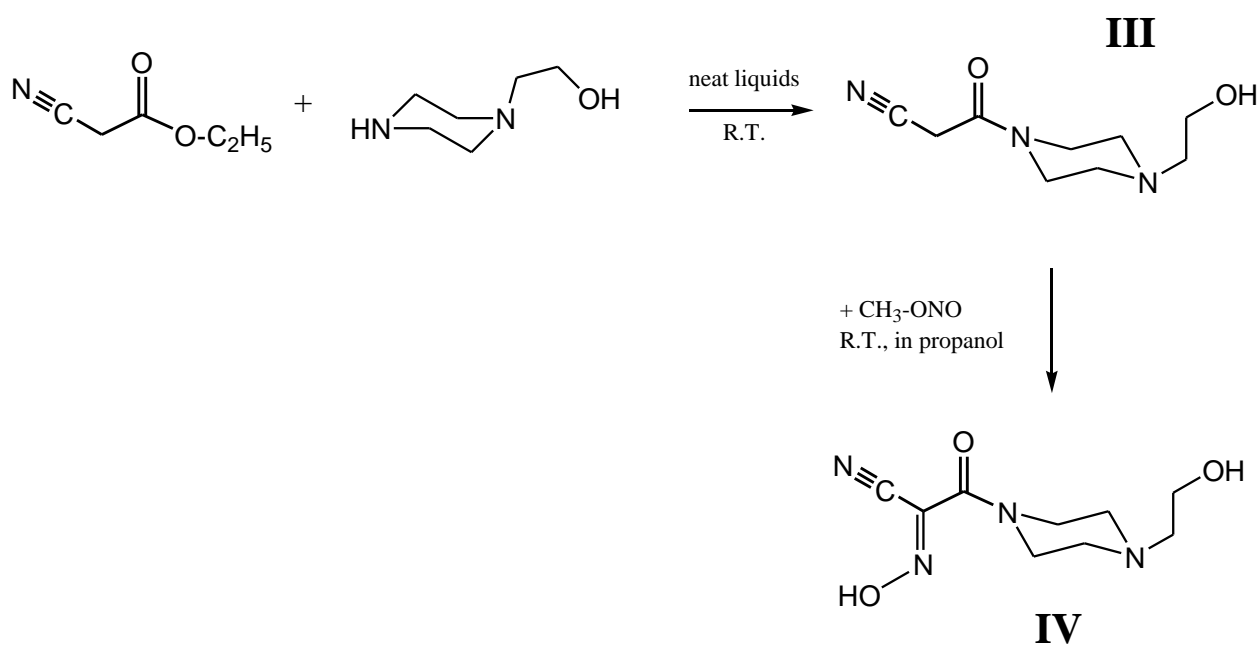


Figure 4. Proposed synthetic route to another, more water soluble cyanoxime ligand **IV**.

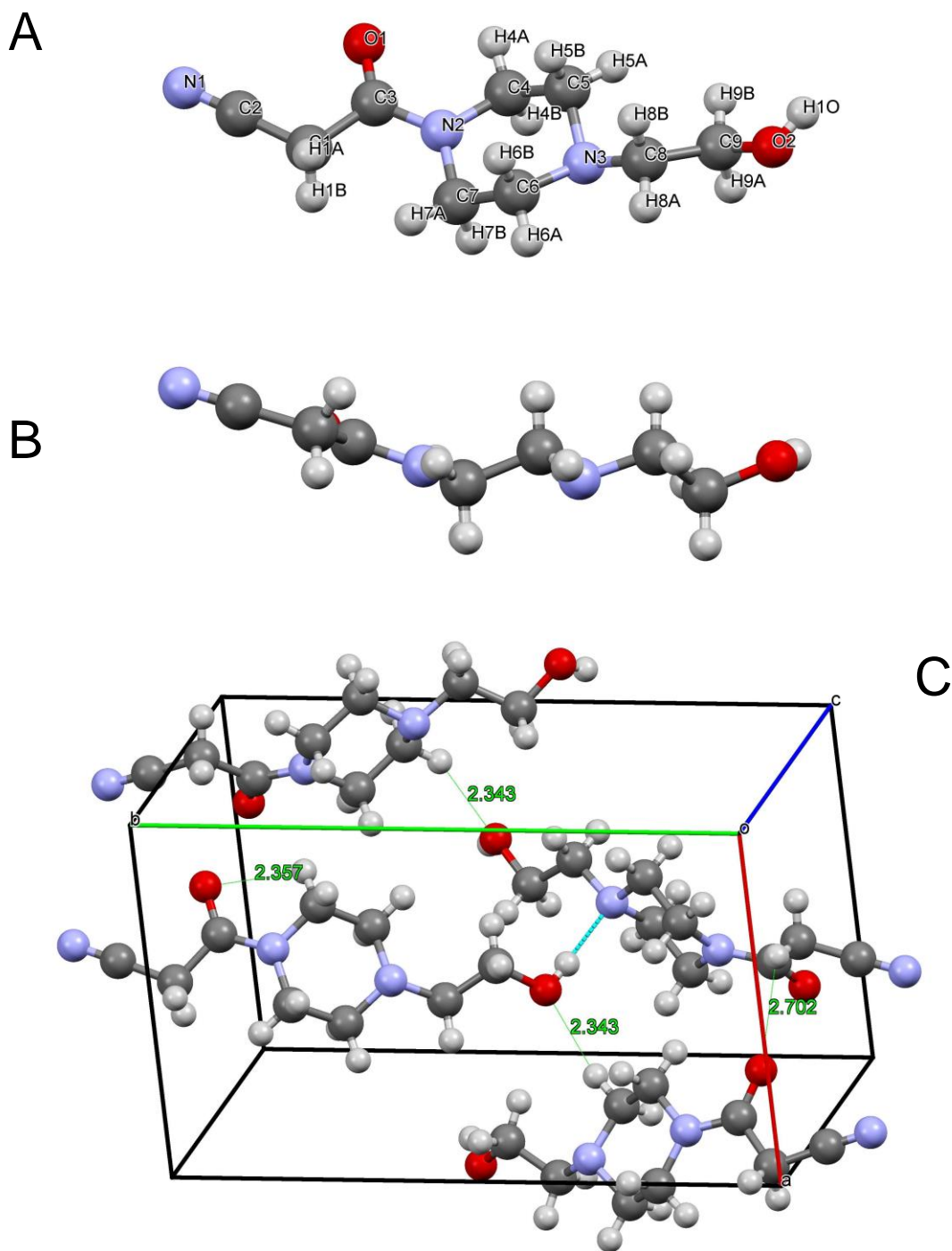


Figure 5. Molecular structure and numbering scheme for the 2-Cyanomethyl-N-ethoxy-piperazine acetamide (A), showing chair conformation of the heterocycle (B), and unit cell content with shortest intermolecular contacts (C).

Crystal data: T=120 K; $Pca2_1$; R1 = 4.1%; GOF = 1.01.

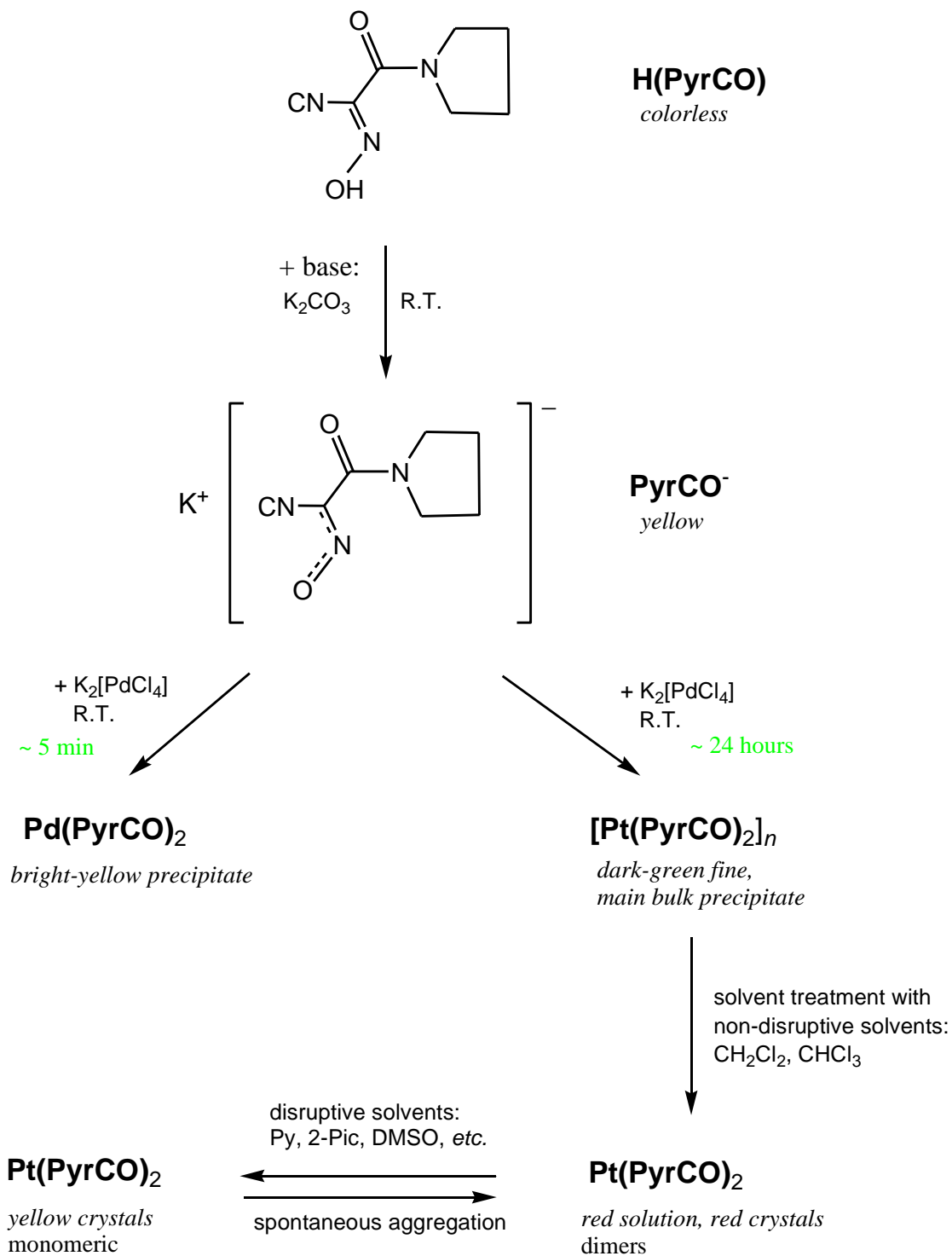


Figure 6. Synthetic route to Pd,Pt-derivatives of the H(PyrCO).

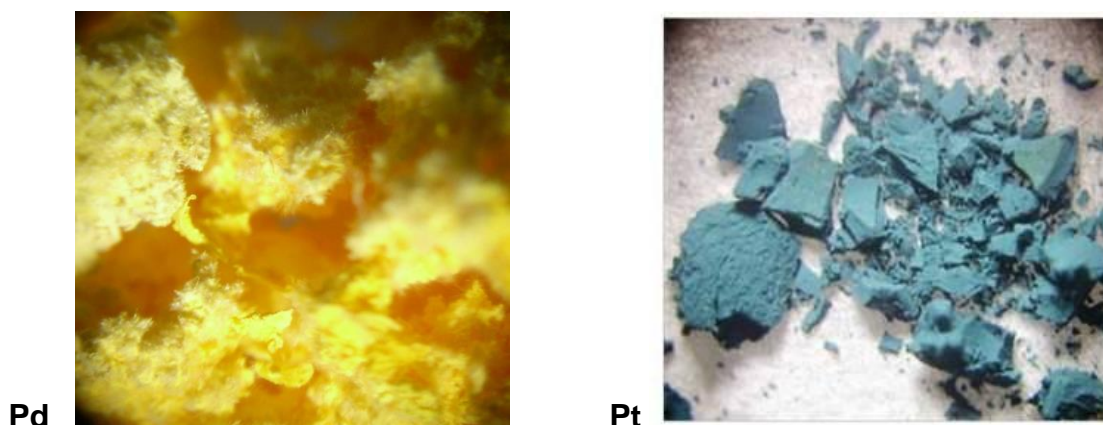


Figure 7. Actual photographs of Pd(PyrCO)₂ and dark-green polymeric [Pt(PyrCO)₂]_n.

Ryan's work was very impressive and much appreciated. I offered Ryan a place in my research group for continuation of already a very successful work on the project and pursuing the MS degree. Unfortunately, due to his family reasons (his infant daughter and ex-wife's health) he declined my offer and left Missouri State University with BS degree only.

Conference presentation with Ryan Kemp:

Spring 2012 National Meeting of the ACS:

Ryan Kemp, Nikolay Gerasimchuk " Synthesis, spectroscopic and structural characterization of a series of novel N-substituted acetamide-cyanoximes and their Pd,Pt complexes." Abstracts of Papers, 243rd ACS National Meeting, San Diego, CA, USA, March 25-29, 2012, INOR-796.

There will be two papers written with Ryan Kemp co-authorship when full characterization of Pt-complexes will be completed.

Group tour to San Diego for the national American Chemical Society spring conference, March 2012

