

Recently we have refined in-house data on the elegant doubly-bound oligomer-tweezer ('zigzag') complex shown. The crystal structure provides the first unequivocal model for chain-folding and small-molecule binding in any synthetic polymer system. Moreover, the supramolecular geometry found in the solid state is remarkably consistent with extensive NMR studies of tweezer-binding in solution. The crystal contains very large solvent cavities and both model building and structure-refinement required very high quality diffraction data. The work was recently accepted for publication in *Nature Chemistry* [1].

[1] Sequence-selective assembly of tweezer molecules on linear templates enables frameshift-reading of sequence information, Z.Zhu, C.J. Cardin, Y. Gan and H.M. Colquhoun, *Nature Chemistry* 2010, (NCHEM 699).

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Copper Based Oxidation Catalysis. T.J. Muller, G. Steyl, A. Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa.*
E-mail: Muller.Theunis@gmail.com

The aerobic oxidation of substituted phenols as a research topic plays an important role in synthesis and biological systems. The demand for value added derivatives of phenolic compounds is steadily growing in the world market, with benzoquinone derivatives constituting a key intermediate in the industrial production of Vitamin E [1]. The use of dioxygen as oxidant is environmentally friendly and available in bulk from the atmosphere. Dioxygen can be catalytically activated by first row transition metal complexes (Cu(II), Co(II) and Mn(IV)) [2]. The addition of co-catalysts (LiCl or MgCl₂) can significantly increase the reactivity of these catalysts during the oxidation cycle [3].

In the current study, model catalyst precursors containing O,O bidentate ligand systems such as tropolone and 2-methyl-3-hydroxy-4-pyrone derivatives, which form five-membered chelates, have been synthesized and structurally characterized and will be discussed. Different aspects of the dioxygen oxidation of selected organic substrates by these copper(II) catalysts, as well as a proposed mechanism for the process, will also be presented.

[1] Sun, H.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.*, 2004, 126, 9550. [2] Simandi, L.I. *Catalytic Activation of Dioxygen by Metal Complexes, Catalysis by Metal Complexes*, 1992, 13, 10. [3] Brenner, W. *German Patent Hoffman-La Roche*, 1972, 2(221), 624

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Influence of Substituents on PhonyH and its Associated Rh(I) Carbonyl Complexes. Gertruida J.S. Venter, Gideon Steyl, Andreas Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa.*
E-mail: truidie@hotmail.com

X-PhonyH (X = aromatic substituents; PhonyH = 4-(phenylamino)pent-3-en-2-one) compounds belong to the group of enaminoketones. Since these contain nitrogen and oxygen

donor atoms as well as an alkene functionality, these electron-rich compounds are of interest in various areas, including application as liquid crystals [1], in fluorescence studies [2], the medical field [3,4] and with significant potential in homogeneous catalysis [5].

This study is therefore concerned with the synthesis of PhonyH derivatives as ligand system and the influence of halide substitution on such ligands with regard to rhodium(I) complex formation. A range of thirteen crystal structures of the (i) free ligands, (ii) complexes of the type [Rh^I(X-Phony)(CO)₂] (X-Phony = 4-(phenylamino)pent-3-en-2-onato derivatives), and (iii) [Rh^I(X-Phony)(CO)(PPh₃)] (substitution of a CO group in (ii) by PPh₃) complexes [6, 7] as catalyst precursors will be discussed. Furthermore, iodomethane oxidative addition, as key step in the catalytic cycles of olefin hydroformylation and methanol carbonylation and the influence of structure/ reactivity relationships therein, will be highlighted.

[1] Pyżuk, W.; Krówczynski, A.; Górecka, E. *Mol. Cryst. Liq. Cryst.* 1993, 237, 75-84. [2] Xia, M.; Wu, B.; Xiang, G. *J. Flu. Chem.* 2008, 129, 402-408. [3] Tan, H.Y.; Loke, W.K.; Tan, Y.T.; Nguyen, N.-T. *Lab Chip* 2008, 8, 885-891. [4] Fanshawe, W.J.; Crawley, L.S.; Safir, S.R.; Wiegand, G.E.; Cooley, E.C. *Substituted enaminoketones*, 1974, US3997530 (Patent). [5] Nair, V.A.; Suni, M.M.; Sreekumar, K. *Proc. Indian Acad. Sci. (Chem. Sci.)* 2002, 114, 481-486. [6] Venter, G.J.S.; Steyl, G.; Roodt, A. *Acta Cryst* 2009, E65, m1321-m1322. [7] Venter, G.J.S.; Steyl, G.; Roodt, A. *Acta Cryst* 2009, E65, m1606-m1607.

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