

Poster Sessions

Only a few crystal structures of these complexes with O,O' bidentate ligand systems are published. Also, very few kinetic studies have been undertaken on these fascinating complexes [9-10]. Alberto et al. [11] focussed on the pH dependence of different polymeric species of the rhenium, but very little attention has been given to the substitution kinetics of these tricarbonyl compounds.

Crystal structures of the aqua substituted Re(I) tricarbonyl complexes with various monodentate incoming ligands, thus the kinetic end products, were obtained and will be discussed in this presentation.

The current available knowledge of these Re(I) tricarbonyl complexes were expanded and contributed to the pool of available crystallographic data.

[1] R. Alberto, R. Schibli, R. Waibel, U. Abram, A.P. Schubiger, *Coord. Chem. Rev.* **1999**, 192, 901. [2] M. Schutte, H.G. Visser, *Acta Cryst.* **2008**, E64, m1226-m1227. [3] M. Schutte, H.G. Visser, A. Brink, *Acta Cryst.* **2009**, E65, m1575-m1576. [4] R. Alberto, R. Schibli, P.A. Schubiger, U. Abram, T.A. Kaden, *Polyhedron* **1996**, 15, 1079. [5] U. Abram, S. Abram, R. Alberto, R. Schibli, *Inorg. Chim. Acta.* **1996**, 248, 193. [6] R. Schibli, R. Alberto, U. Abram, S. Abrams, A. Egli, P.A. Schubiger, T.A. Kaden, *Inorg. Chem.* **1998**, 37, 3509. [7] R. Alberto, A. Egli, R. Schibli, U. Abram, T.A. Kaden, A.O. Schaffland, R. Schwarzath, P.A. Schubiger, *Q. J. Nucl. Med.* **1998**, 42, 9. [8] S. Mundwiler, M. Kundig, K. Ortner, R. Alberto, *Dalton Trans.* **2004**, 1320. [9] B. Salignac, P.V. Grundler, S. Cayemittes, U. Frey, R. Scopelliti, A.E. Merbach, *Inorg. Chem.* **2003**, 42, 3516. [10] L. Helm, *Coord. Chem. Rev.* **2008**, 252, 2346. [11] R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich, P.A. Schubiger, *J. Chem. Soc. Dalton Trans.* **1984**, 2815.

Keywords: Kinetics, Rhenium

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Enaminoketones: Influencing Rh(I) dicarbonyl complexes with halogen substituents

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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 $[\text{Rh}^{\text{I}}(\text{X-Phony})(\text{CO})_2]$ (X-Phony = 4-(phenylamino)pent-3-en-2-onato derivatives), and (iii) $[\text{Rh}^{\text{I}}(\text{X-Phony})(\text{CO})(\text{PPh}_3)]$ (substitution of a CO group in (ii) by PPh_3) 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] W. Pyżuk, A. Krówczynski, E. Górecka, *Mol. Cryst. Liq. Cryst.* **1993**, 237, 75-84. [2] M. Xia, B. Wu, G. Xiang, *J. Flu. Chem.* **2008**, 129, 402-408. [3] H.Y. Tan, W.K. Loke, Y.T. Tan, N.-T. Nguyen, *Lab Chip* **2008**, 8, 885-891. [4] W.J. Fanshawe, L.S. Crawley, S.R. Safir, G.E. Wiegand, E.C. Cooley, *Substituted enaminoketones* **1974**, US3997530 (Patent). [5] V.A. Nair, M.M. Suni, K. Sreekumar, *Proc. Indian Acad. Sci. (Chem. Sci.)* **2002**, 114, 481-486. [6] G.J.S. Venter, G. Steyl, A. Roodt, *Acta Cryst* **2009**, E65, m1321-m1322. [7] G.J.S.

Venter, G. Steyl, A. Roodt, *Acta Cryst* **2009**, E65, m1606-m1607.

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Measuring selectivity in host-guest systems

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When a host compound, H, is dissolved in a mixture of liquid guest A and B to form inclusion compounds



then one may write the equilibrium constants

$$K_1 = [\text{H} \cdot \text{An}] / [\text{H}] [\text{A}]^n \quad K_2 = [\text{H} \cdot \text{Bm}] / [\text{H}] [\text{B}]^m$$

with the standard state defined as 1 mol dm⁻³.

The selectivity of the host H is given as the ratio of the equilibrium constants

$$\text{selectivity} = K_1 / K_2$$

However, if the host forms an inclusion compound which incorporates both guests



where generally $n \neq m'$, $m \neq m'$, then the selectivity cannot be so defined.

We have therefore elected to employ the selectivity coefficient

$$K_{\text{A:B}} = (K_{\text{B:A}})^{-1} = Z_{\text{A}} / Z_{\text{B}} * X_{\text{B}} / X_{\text{A}} [1]$$

where X_{A} , X_{B} are the mole fractions of the guest in the mother liquor and Z_{A} , Z_{B} are the mole fractions in the resulting crystal.

We have studied a series of host-guest systems comprising bulky diol-hosts with pairs of related guests and have measured their selectivity curves. The results are rationalised by NMR results, crystal structure analysis, examination of the non-bonded interactions and evaluation of the volume of the voids which accommodate the guest molecules.

Examples are given of poor versus good selectivity as well as when the selectivity is concentration dependent, giving rise to sigmoid selectivity curves. We demonstrate the possibility of mapping the enclathration process of a four dimensional system, comprising the host H and three competing guests A, B and C.

[1] A.M. Pivovar, K.T. Holman, M.D. Ward, *Chem. Mater.* **2001**, 13, 3018.

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Dinuclear Gadolinium(III) complexes constructed by monocarboxylate ligands

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The chemistry of gadolinium(III) carboxylate complexes, especially those with direct interaction between Gd(III) centres, has been the