s13.m38.o4 Towards the Synthesis of Supramolecular Polygons and Polyhedra Containing the Ruthenium-η⁶-Arene Unit. Sophie H. Dale and Mark R. J. Elsegood, Chemistry Department, Loughborough University, Loughborough, LE11 3TU, UK. E-mail: S.H.Dale@lboro.ac.uk

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Stang et al [1] and Zaworotko et al [2] have investigated the synthesis of supramolecular polygons and polyhedra from coordination complexes bearing a combination of site-blocking and linker-style ligands, while this has been extended by Yamamoto et al [3] to include functional, organometallic metal(η^6 -arene) units in the synthesis of supramolecular rectangles. The dimeric $[Ru(\eta^6-arene)X_2]_2$ (X = halide; arene = benzene, p-cymene, hexamethylbenzene etc.) complexes are important reagents in the synthesis of further substituted $\operatorname{Ru}(\eta^6$ -arene) complexes through the lability of the bridging Ru-X bonds [4,5], yielding sandwich or piano-stool complexes. Pyridinepolycarboxylic acids possess aromatic N-functionality ideal for coordination to the Ru(η^6 -arene) unit, leaving uncoordinated carboxylic acid groups available for hydrogen bonding interactions. Neutral, pseudo-octahedral complexes of the form $\operatorname{Ru}(\eta^6-p$ -cymene)(N,O-L-L)X [where N,O-L-L = pyridine-2-carboxylate or *n*-carboxy-pyridine-2-carboxylate (*n* = 3, 4 or 5) and X = Cl, Br or I] are formed readily from the reaction of $[\operatorname{Ru}(\eta^6-p-\operatorname{cymene})X_2]_2$ with two equivalents of the required pyridinecarboxylic acid. A range of cationic species $[\operatorname{Ru}(\eta^6-p\text{-cymene})(N,O-L-L)L']+$ (where L' = monodentate ligand) are synthesised through the removal of chloride from $[Ru(\eta^6-p-cymene)Cl_2]_2$ prior to reaction with the desired N,O-bidentate and monodentate ligands. Structural examples from this diverse system will be presented, including complexes which have crystallised as chains, ladders and discrete quadrangles through the formation of intermolecular hydrogen bonded arrays.



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s13.m38.o5 Cluster-based catalysts for asymmetric synthesis. Viktor Moberg and Ebbe Nordalnder, Inorganic Chemistry, Chemical Center, Lund University, Box 124, S-221 00 Lund, Sweden. E-mail: viktor.moberg@inorg.lu.se

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It is known that transition metal clusters are efficient catalysts in several types of chemical reactions of metal cluster chemistry. Surprisingly, very few investigations involve studies of asymmetric synthesis.¹ We are currently studying the use of transition metal carbonyl clusters as catalysts (or stoichiometric reagents) for asymmetric reactions.² Chirality is introduced via chiral ligands, in particular chiral monodentate phosphines and diphosphines. Clusters of the didentate type $[H_4Ru_4(CO)_{12-2n}(P-P)_n]$ (n=1,2; P-P = diphosphine) (see Figure 1) have been found to be particularly efficient catalysts for asymmetric reactions, in particular hydrogenation of α-unsaturated carboxylic acids. In certain cases, enantiomeric excesses (ee's) of 70-80% have been obtained. Evidence indicates that it is indeed the clusters that act as catalysts, i.e. they are not precursors for mononuclear active species.



Figure 1: ORTEP plot of $[H_4Ru_4(CO)_{10}-1,2-(R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)ferrocenyl]ethyldi(bis-3,5-trifluoro-methylphenyl)phosphine)]$

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