

**Figure 1.** *ORTEP* diagram of  $[\text{Fe}(\text{TpivPP})(\text{NCO})]^-$  ion complex showing thermal ellipsoids at 30 % probability level.

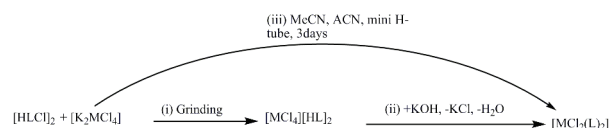
**Keywords:** porphyrins; cyanato-*N* iron(II); X-ray molecular structure

#### FA4-MS06-P24

**Solid State Preparation of Palladium-carbene Complexes.** Emily M. Mutambi<sup>a</sup>, Christopher J. Adams<sup>a</sup>, A. Guy Orpen<sup>a</sup>. <sup>a</sup>*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK.*

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There is great interest in palladium complexes as catalysts, and over the past ten years the number of palladium complexes of *N*-heterocyclic ligands has rapidly increased. [1] There is an enormous amount of data currently available on NHC chemistry, and methods for the synthesis of NHCs and their metal complexes are regularly reported.[2,3] Synthetic procedures leading to precursor imidazolium salts have been elucidated including the development of many routes that allow the introduction of an NHC ligand to a metal centre.[4] As part of our ongoing research in this area we will report the synthesis of a number of new palladium complexes incorporating sterically bulky carbene ligands which have been prepared in bulk by solid state methods (Scheme 1), with single crystals grown by employing crystal growing techniques using solution methods. The powder patterns of the two different techniques have been compared to prove that the bulk material prepared in solid state is a true representation of the desired product.



**Scheme 1:** Synthetic route for the palladium-carbene complexes: (i) direct grinding with HLCl; (ii) mechanochemical elimination of HCl (grinding with KOH/K<sub>2</sub>CO<sub>3</sub>/KOBu<sup>t</sup>); and (iii) Preparation

of the palladium complexes by solution methods; L=Ligand

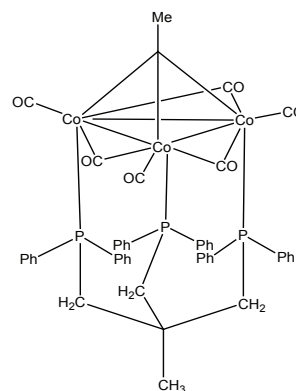
[1] C. P. Newman, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organomet.*, **2007**, 26, 6225-6233. [2] C. P. Newman, G. J. Clarkson and J. P. Rourke, *J. Organomet. Chem.*, **2007**, 692, 4962-4968. [3] R. A. Moss, L. Wang, E. Weintraub and K. Krogh-Jespersen, *J. Phys. Chem. A*, **2008**, 112, 4651-4659. [4] W. Wei, Y. C. Qin, M. M. Luo, P. F. Xia and M. S. Wong, *Organomet.*, **2008**, 27, 2268-2272.

**Keywords:** solid state; N-heterocyclic ligands; palladium

#### FA4-MS06-P25

**Preparation and Structures of  $\text{RCCo}_3(\text{CO})_6$  (triphos) clusters** [R = Me, Ph, CO<sub>2</sub>Et, Fc]. Jim Simpson<sup>a</sup>, C. John McAdam<sup>a</sup>, Brian H. Robinson<sup>a</sup>, Roderick G. Stanley<sup>a</sup>. <sup>a</sup>*Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, 9054, New Zealand.*  
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In simple methinyltricobaltnonacarbonyl clusters,  $\text{RCCo}_3(\text{CO})_9$ , six of the carbonyl ligands occupy equatorial sites, close to the plane of the triangle of cobalt atoms with the other three carbonyl groups approximately orthogonal to that plane in axial positions. Monodentate or bidentate phosphine or phosphite ligands almost invariably substitute carbonyl groups from equatorial sites. Furthermore, the remaining equatorial carbonyl ligands generally adopt terminal conformations; carbonyl bridging of the Co—Co bonds is found only in situations where the apical substituent R, or the substituting ligands, significantly increase the electron density on the  $\text{CCo}_3$  cluster core.



We are interested in the coordination behaviour of the potentially tridentate 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos), as its chemistry is relatively underdeveloped, particularly in organometallic compounds. The ligand reacts readily with various tricobalt carbon clusters in refluxing petroleum ether/acetone to replace three carbonyl ligands and give the resulting  $\text{RCCo}_3(\text{CO})_6$  (triphos) complexes in moderate yields. X-ray quality crystals of four of these products have been obtained and their structures will be reported. The triphos ligand coordinates with its P atoms occupying axial sites on the  $\text{CCo}_3$  core and the build-up of electron density accompanying this substitution results

in three of the equatorial CO ligands adopting bridging conformations.

**Keywords: cobalt clusters; tridentate phosphine; single-crystal structure analysis**

#### FA4-MS06-P26

**Crystal structures of  $\text{Ln}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$  ( $\text{Ln} = \text{Pr}, \text{Sm}$ ) and  $\text{Ce}_3\text{O}[\text{AsO}_3]_2\text{Cl}$ .** Hamdi Ben Yahia<sup>a</sup>, Ute Ch. Rodewald<sup>a</sup>, Rainer Pöttgen<sup>a</sup>. <sup>a</sup>*Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany.*

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The title compounds with structures isotopic to the  $\text{Nd}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$  [1] and  $\text{Gd}_3\text{O}[\text{AsO}_3]_2\text{Cl}$  [2] types have been synthesised. The crystal structures of  $\text{Pr}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$ ,  $\text{Sm}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$  and  $\text{Ce}_3\text{O}[\text{AsO}_3]_2\text{Cl}$  were determined using single crystal data. The compounds  $\text{Ln}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$  have monoclinic unit cell parameters:  $a = 12.493(3)$  Å,  $b = 5.5884(13)$  Å,  $c = 9.0776(19)$  Å,  $\beta = 116.610(14)^\circ$  and  $a = 12.2528(26)$  Å,  $b = 5.6101(9)$  Å,  $c = 8.9059(20)$  Å,  $\beta = 115.945(16)^\circ$  for the Pr and Sm compounds, respectively. Both crystallize with space group  $C2/m$ ,  $Z = 2$  whereas  $\text{Ce}_3\text{O}[\text{AsO}_3]_2\text{Cl}$  crystallises in space group  $P4_2nm$ ,  $Z = 4$  with unit cell parameters  $a = 12.8590(6)$  Å,  $c = 5.5627(3)$  Å. The structure of  $\text{Ln}_5\text{O}_4[\text{AsO}_3]_2\text{Cl}$  contains three crystallographically independent  $\text{Ln}^{3+}$  sites with 8, 7 and 8 coordinated  $\text{Ln}^{3+}$  atoms whereas the  $\text{Ce}_3\text{O}[\text{AsO}_3]_2\text{Cl}$  structure contains only two  $\text{Ce}^{3+}$  sites with 6 and 8 coordinated cerium atoms. The common features to these structures are isolated pyramidal  $[\text{AsO}_3]^{3-}$  anions with a stereochemically active non-bonding electron pair.

[1] Kang D.-H., Wontcheu J., Schleid Th., *Solid State Sci.* **2009**, 11, 299. [2] Kang D.-H., Komm Th., Schleid Th., *Z. Kristallogr. Suppl.* **2005**, 22, 157.

**Keywords: lanthanoide oxide chloride oxoarsenate(III); crystal structure determination; single crystal diffraction**