Recent developments in lanthanoid pseudo-Grignard reagent chemistry

Professor **Peter C. JUNK**

School of Pharmacy & Molecular Sciences, James Cook University,
Townsville, Qld, 4811, Australia – *e-mail:* peter.junk@jcu.edu.au

We have progressed metal based syntheses using rare earth metals considerably over the past several years. Organo-mercury and -thallium reagents have been extremely versatile reagents in redox transmetallation (equation 1) while the mercury reagents have also found great utility in the more convenient redox transmetallation/protolysis reactions (equation 2).[1] We have now extended this rare earth chemistry to the use of less toxic reagents such as $RSnMe_3$,[2], $BiPh_3$,[3] and most recently using pseudo-Grignard type chemistry[4] (equation 3) and use of I_2 to activate the metal (equation 4).[5] This presentation will involve a discussion of the latter two methods.
In lanthanoid pseudo-Grignard chemistry, we have been able to use these reagents in protolysis reactions to deliver heteroleptic iodo(metal organic)lanthanoid species in good yield,[4] despite previous reports of the mixed oxidation state for PhLnI (Ln = Eu, Yb).[5] The species obtained our attempts to crystallise "$PhYbI(thf)_n$" complexes will be presented.
We have recently shown that bulk lanthanoid metal can be activated by a few % of iodine crystals in the presence of a protic ligand to produce metal-organic compounds (equation 4). In this presentation, the new directions of the project will be discussed along with the most recent exciting results.

$$RE + ML_n \rightarrow RE(L)_n + M\downarrow \quad (RE = \text{rare earth; } M = Hg, Tl, n = 2,3) \qquad (1)$$

$$RE + ML'_n + nLH \rightarrow RE(L)_n + M\downarrow + nL'H \qquad (2)$$

$$\text{“RREI(solv)n”} + LH \rightarrow [RE(L)I(solv)_4] + RH \qquad (3)$$

$$RE(I_2) + nHL \xrightarrow{\text{thf or dme}} [RE(L)_n(solv)_m] + n/2H_2 \quad (n = 2, 3) \qquad (4)$$

[1] G.B. Deacon *et al*., J. Organomet. Chem., **647**, 50 (2002).
[2] S Beaini, GB Deacon, M Hilder, PC Junk and DR Turner, Eur. J. Inorg. Chem., 3434 (2006).
[3] M.M. Gillett-Kunnath, J.G. MacLellan, C.M. Forsyth, P.C. Andrews, G.B. Deacon and K. Ruhlandt-Senge, Chem. Commun., 4490 (2008).
[4] M Wiecko, GB Deacon and PC Junk, Chem. Commun., **46** 5076 (2010).
[5] D.F. Evans *et al.,* J. Chem. Soc. D., 244 (1970; J. Chem. Soc. A., 1931 (1971)

Funding for this work provided by The Australian Research Council (DPDP0984775)