Solventless Organometallic Chemistry

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Novel approaches to waste disposal and atom economy are being incorporated into synthetic chemistry. The simplest approach to these issues is to perform reactions in the absence of solvents. While in principle this appears a trivial solution to an environmental problem, complicating factors relating to diffusion, heat and mass transfer etc. have to be addressed. These factors may yield different reaction mechanisms and either aid or reduce the activity/selectivity of the process. Our approach has been to evaluate solventless reactions via the study of well-established organometallic chemistry reactions This has included the study of reactions in the *solid-state* and in the *melt* and include (i) substitution reactions ($Mn(CO)_4(PPh_3)Br$ + PPh_3 to give $Mn(CO)_3(PPh_3)_2Br$) (ii) insertion/migration reactions (e.g. $CpRMo(CO)_3R'$ + L to give $CpRMo(CO)_2L(COR')$) (iii) de-insertion (e.g. $CpRMo(CO)_2L(COR')$ to $CpRMo(CO)_2LR'$) reactions and isomerisation reactions (e.g. cis/trans-$CpRe(CO)(L)Br_2$). All the above occur in the absence of solvents. A comparison will be made with solution studies and the influence of steric/electronic ligand effects on the reaction will be highlighted. Techniques that have been used to generate data include optical microscopy, DRIFTS and DSC.