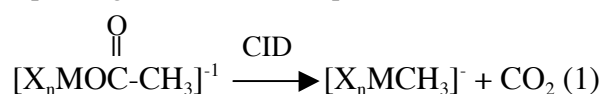


Ligand Effects in gas phase ion-molecule reactions of Grignard and Organocuprate reagents.

Patrick F. James, Richard A.J. O'Hair*, Ana K. Vrkic

School of Chemistry, University of Melbourne, Melbourne, Victoria, AUSTRALIA

Introduction: Ligand effects have been observed in the condensed phase reactions of Grignard [1] and organocuprate reagents [2]. Their origins remain obscure due to the uncertainties regarding the structure(s) of the reactive organometallic. This presentation aims at unraveling ligand effects by examining the gas phase reactivity of anionic organometallic reagents using a quadrupole ion trap. Species such as Grignard reagents and organocuprates are formed in the gas phase via decarboxylation of the corresponding metal acetates (eq. 1) [3].



Methods and Instrumentation: Electrospray ionization (ESI) of simple metal acetates $[\text{Metal}(\text{CH}_3\text{CO}_2)_n]$ generates several species including $[\text{Metal}(\text{CH}_3\text{CO}_2)_{n+1}]^{-1}$ ions. Using multi-stage mass spectrometry experiments in a modified ion trap (LCQ), these anions can be subjected to CID and the resultant organometallic anions can be mass selected and subject to additional stages of CID or ion-molecule reactions with neutral reagents such as methanol and methyl iodide. By varying the reaction time, rate measurements can be made to compare reactivity trends.

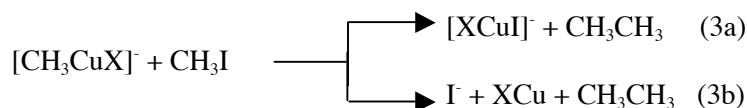
Results:

(1) **Ligand Effects in Grignard reactions.** Grignard reagents undergo reactions typical for such a species (eq. 2). Reactivity towards water is attenuated for the acetate ligand, consistent with DFT calculations, which suggest that steric effects play a role.



R	X	Efficiency	Transition State Energy versus Separated Reactants (kcal/mol)
H	CH ₃ CO ₂	0.07	-2.5
H	Cl	0.52	-6.3

(2) **Ligand Effects in organocuprate reactions.** This organocuprate reagent undergoes a typical coupling reaction with CH₃I (eq. 3). Deuterium labeling experiments reveal that this reaction does not exhibit cross-coupling while significant ligand effects are observed. DFT calculations reveal two mechanisms: (a) a side on S_N2 reaction; (b) a "T-like" S_N2 reaction.



X	Efficiency
CH ₃ CO ₂	0.0007
CH ₃	0.03

References:

- (1) M. T. Reetz, N. Harmat, R. Mahrwald, *Angew. Chem. Int. Ed.*, 1992, 31, 343
- (2) E Nakamura, S Mori, *Angew. Chem. Int. Ed.*, 2000, 39, 3754; E Nakamura, M Yamanaka, *J. Am. Chem. Soc.*, 1999, 121, 8941
- (3) R.A.J O'Hair, *Chem. Comm.*, 2002, 20; R.A.J O'Hair, Proc. 50th ASMS Conf. Mass Spectrom. Allied Topics, Marriott World Center, Orlando, Florida, June 2-6, 2002.