

Solvent-free Substitution Reactions of Solid Phosphines with $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$ (R = H, Me) Complexes

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Z. Naturforsch. **2007**, 62b, 453 – 459; received November 1, 2006

Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday – friend and colleague over many decades

Reactions of $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$ (R = H, Me) complexes with phosphine ligands PR'_3 (R' = Ph, *m*-Tol, *p*-C₆H₄OMe, *p*-C₆H₄Cl, *p*-C₆H₄F) have been performed under solvent-free conditions in the melt phase and generally yielded the ionic products $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{PR}'_3]\text{I}$ rather than the CO substituted products $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PR}'_3)\text{I}$. The complexes have been characterised by IR, NMR and MS techniques. By contrast, the same reactions studied in benzene solution have yielded mainly the CO substitution products. Factors that affect the solvent-free reaction include variation in R and R', reaction temperature and the addition of $[\text{CpFe}(\text{CO})_2]_2$ as a catalyst. The mechanism of the reaction for the formation of the ionic complex is proposed to go *via* a 19 electron intermediate. This is in contrast to the reaction in benzene that occurs *via* a 17 electron intermediate, clearly indicating the role of the melt phase in the reaction.

Key words: Melt Phase, Solvent-free Reaction, Iron Cyclopentadienyl Complex, Metal Dimer Catalyst, Green Chemistry