Effect of Ligands on Copper-promoted Hydride Transfer to Carbonyl Group

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Summary The effect of ligands on hydride transfer to a carbonyl group (Tishchenko reaction and Meerwein-Ponndorf reduction) caused by Bu^{t}OCu complexes is described.

A VARIETY of ligands have been used in copper-promoted reactions, but their effect on the reactivity of copper-complexes has not been studied. On the basis of our recent work on the isolation of Bu^{t}OCu·L complexes [L = PEt$_3$, P(OMe)$_3$, Bu^{t}NC and CO],[1,2] we now report the effect of various ligands on hydride transfer to a carbonyl group caused by Bu^{t}OCu complexes. This reaction is the first example of copper-promoted hydride transfer to a carbonyl group,[3] although reactions by aluminum alkoxide are well known (Tishchenko reaction and the Meerwein-Ponndorf reduction).

The Tishchenko reaction was carried out on benzaldehyde at room temperature in THF in the presence of Bu^{t}OCu and an equimolar amount of an appropriate ligand to give benzyl benzoate. Without the ligand, Bu^{t}OCu did not induce the reaction. In the reaction catalysed by Bu^{t}OCu–PBu$^n_3$, a stoicheiometric material balance was attained; the reaction mixture after treatment with water consisted of unchanged benzaldehyde (40%), benzyl benzoate (40%), benzyl alcohol (11%) and t-butyl benzoate (12%). The yields of benzyl benzoate after 48 h reaction time with various ligands were Bu$^n_3$P 83, Ph$_3$P 68, Bu^{t}NC 61, (MeO)$_3$P 49, C$_5$H$_5$N 30, Et$_3$N 27 and CO 0%. This order also indicates the effect of the ligand upon some nucleophilic reactions *e.g.* the addition of cuprous alkoxide to a carbonyl group followed by the transfer of β-hydrogen as a hydride from the resulting cuprous s-alkoxide.

The Meerwein-Ponndorf reduction was carried out using Bu^{t}OCu–phosphine complexes and the effect of the phosphine ligand on the hydride transfer step was evaluated. After a quantitative alcohol exchange with Bu^{t}OCu-phosphine complexes, borneol reduced benzophenone to produce benzhydrol after hydrolytic work up. The yields of benzhydrol were dependent upon the phosphine ligands and were Bu$^n_3$P 33, Ph$_3$P 25, and (MeO)$_3$P 20%, in a reaction using Bu^{t}OCu (1 mM), phosphine (1 mM), borneol (2 mM), and benzophenone (5 mM) in 4 ml THF at 80° for 48 h.

In general, the electronic effect of the ligand is discussed in terms of a combination of the σ-donating and π-accepting abilities of the ligand.[4] In the hydride transfer reaction, we conclude that a σ-donating ligand promotes the reaction. This can be shown by the increase of the electron density of the alkoxyl group from the strong σ-donor character of the ligand which facilitates the nucleophilic addition of the alkoxyl group and the hydride transfer. In the phosphine homologues of Bu^{t}OCu·L complexes, correlation of the n.m.r. shifts of the Bu^{t}O group with the σ-donor strength of the phosphine ligand has been observed,[2] Bu^{t}OCu·PBu$^n_3$ (τ 8·53), Bu^{t}OCu·PEt$_3$ (τ 8·47) and Bu^{t}OCu·P(OMe)$_3$ (τ 8·38). It is significant to note that the order of the effectiveness of ligands in the present study agrees with the 'spectrochemical series'[5] for π-bonding ligands which shows the extent of variation of positive charge on the central metal caused by the ligand *via* inductive and π-electron accepting mechanisms. This is one of few examples correlating the electronic property of various ligands with the reactivity of copper-complexes.

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