Carbon Dioxide Insertion into Organocopper and Organosilver Compounds

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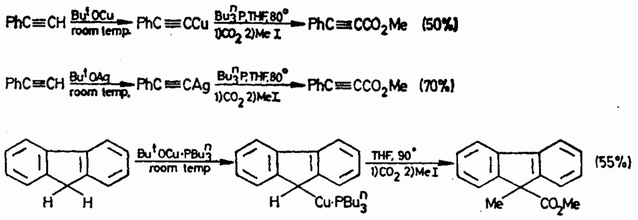
Summary Carbon dioxide insertions into organocopper and organosilver compounds occur in the presence of σ-donor ligands such as $Bu^n{}_3P$ and Bu^tNC which increase the carbanionic reactivity of the organometallics.

Carbon dioxide is known to react with transition metal compounds either with complex formation or CO_2 insertion. However, examples of CO_2 insertion into a transition metal–carbon bond are limited[1] and examination of the factors affecting the CO_2 insertion is important. We now report that when organocopper and organosilver are co-ordinated with a trialkylphosphine or isonitrile ligand with a high σ-donor strength they easily undergo CO_2 insertion into the metal–carbon bond.

The organocopper and organosilver compounds were prepared using Bu^tOCu[2] and Bu^tOAg[3] as metallation agents. The products were isolated and CO_2 insertion carried out in the presence of an equimolar amount of $Bu^n{}_3P$ in THF. (The fluorenylcopper complexes were not isolated before CO_2 insertion). These reactions are the first examples of CO_2 insertion into organocopper and organosilver compounds except for fluorinated organometallics.[4]



The effect of the σ-donor ligands on CO_2 insertion is shown in the Table. $Bu^n{}_3P$, Bu^tNC, and $(MeO)_3P$ solubilize copper and silver phenylacetylides in THF by dissociating their polymeric forms.[5] $(MeO)_3P$ and pyridine

TABLE. Ligand effect upon CO_2 insertion. Yields of the carboxylated products (%)

	$\mathrm{Bu^n{}_3P}$	$\mathrm{Bu^tNC}$	$\mathrm{(MeO)_3P}$	Pyridine	No ligand
Fluorenyl copper	55	trace	trace	trace	0
PhC≡CCu	50	71	4	trace	0
PhC≡CAg	70	65	trace	0	0

Conditions; $\mathrm{Bu^tOCu}$ (~ 0·5 mM) : fluorene : ligand : MeI = 1 : 1·5 : 1 : 3; metal acetylide (~0·3 mM) : ligand : MeI = 1 : 1 : 3.

(in which copper phenylacetylide is partly soluble) were not effective for CO_2 insertion. The effects of these four ligands may be explained in terms of their different σ-donor strengths; $\mathrm{Bu^n{}_3P}$ and $\mathrm{Bu^tNC}$ with higher σ-donor strengths increase the carbanionic reactivity of the alkynyl group to allow the CO_2 insertion. The weaker σ-donor strength of $\mathrm{(MeO)_3P}$ has been demonstrated by the n.m.r. shifts of the $\mathrm{Bu^tO}$ group in $\mathrm{Bu^tOCu{\cdot}PR_3}$ complexes,[6] $\mathrm{Bu^tOCu{\cdot}PBu^n{}_3}$ (τ 8·53), $\mathrm{Bu^tOCu{\cdot}PEt_3}$ (τ 8·47) and $\mathrm{Bu^tOCu{\cdot}P(OMe)_3}$ (τ 8·38).

In fluorene–$\mathrm{Bu^tOCu}$–$\mathrm{Bu^tNC}$, CO_2 insertion did not take place. Instead, $\mathrm{Bu^tNC}$ was inserted into the copper–carbon bond of a fluorenylcopper–isonitrile complex.[7] In fluorene–$\mathrm{Bu^tOCu}$–pyridine, CO_2 insertion was not observed, and the formation of t-butyl alcohol (98%) and metallic copper (77%) suggest the quantitative formation of a fluorenylcopper–pyridine complex which decomposes rapidly without CO_2 insertion. The fluorenylcopper–$\mathrm{P(OMe)_3}$ complex did not give the carboxylated product. For CO_2 insertion into the fluorenylcopper, $\mathrm{Bu^n{}_3P}$ was the most effective ligand.

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