# Synthesis of Formates from Alcohols, Carbon Dioxide, and Hydrogen Catalysed by a Combination of Group VIII Transition-metal Complexes and Tertiary Amines

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*Summary* A novel system composed of group VIII transition-metal complexes and tertiary amines catalyses the formation of formates from alcohols, carbon dioxide, and hydrogen gas.

LITTLE is known about the fixation of carbon dioxide into organic compounds catalysed by transition-metal complexes.[1–3] Methyl formate has been synthesized from MeOH, $CO_2$, and $H_2$ gas in benzene in the presence of a catalyst composed of Ru, Ir, Os, or Pt complexes and $BF_3$.[3]

We report here that some formates can be synthesized from alcohols, $CO_2$ gas, and $H_2$ gas by a new catalytic combination of group VIII low-valent complexes and tertiary amines. Table 1 shows the catalytic formation of methyl, ethyl, and propyl formate from the corresponding

TABLE 1. Formation of alkyl formates from alcohols, $CO_2$, and $H_2$ with $[Pd(diphos)_2]$–$R_3^2N$ catalysts[a]

| $R_3^2N$ | $HCO_2R^1$ yield (mol/mol Pd) | | |
|---|---|---|---|
| | $R^1$ = Me, | Et, | $Pr^n$ |
| $Me_3N$[b] | 23 | 21 | 21 |
| $Et_3N$ | 24 | 15 | 14 |
| $Pr^n{}_3N$ | 33 | 6 | 7 |
| $Bu^n{}_3N$ | 23 | 6 | 7 |
| $Oct^n{}_3N$ | | 6 | 9 |
| *N*-Methylpyrrolidine | | 35 | |
| *N*-Methylpiperidine | | 31 | |
| 1,4-Diazabicyclo[2,2,2]octane | | 37 | |

[a] $[Pd(diphos)_2]$ (0·1 mmol), $R^1OH$ (250 mmol), $R_3^2N$ (25 mmol), $CO_2$ (25 atm at 25 °C), and $H_2$ (25 atm at 25 °C); 140 °C, 21 h. [b] 18 mmol.

alcohols, $CO_2$, and $H_2$ with a combination of $[Pd(diphos)_2]$ and several tertiary amines (diphos = $Ph_2PCH_2CH_2PPh_2$). In the absence of the tertiary amine, this reaction does not occur. Lower trialkylamines are effective as catalyst, higher amines being less effective for ethanol and n-propanol. Cyclic tertiary amines are the most effective. The conditions in Table 1 have not been optimized. Ethyl formate

TABLE 2. Catalytic effect of group VIII metal complexes and $Et_3N$ for ethyl formate synthesis[a]

| Complex | $HCO_2Et$ yield (mol/mol complex) | Complex | $HCO_2Et$ yield (mol/mol complex) |
|---|---|---|---|
| $[H_2Fe(diphos)_2]$ | 2 | $[H_2Ru(PPh_3)_4]$ | 26 |
| $[HCo(diphos)_2]$ | 5 | $[RhCl(PPh_3)_3]$ | 30 |
| $[(HCO_2)Co(PPh_3)_3]$ | 2 | $[H_3Ir(PPh_3)_3]$ | 18 |
| $[Ni(diphos)_2]$ | 1 | $[Pt(PPh_3)_4]$ | 4 |

[a] Complex (0·1 mmol), EtOH (250 mmol), $Et_3N$ (25 mmol), $CO_2$ (25 atm at 25 °C), and $H_2$ (25 atm at 25 °C); 140 °C, 21 h.

{58 mol per mol of $[Pd(diphos)_2]$} was formed at 160 °C after 20 h under an initial pressure of 30 atm of $CO_2$ and 70 atm of $H_2$ with 0·1 mmol of $[Pd(diphos)_2]$, 100 mmol of $Et_3N$, and 250 mmol of EtOH; *ca.* 59 mol of $H_2O$ per mol of $[Pd(diphos)_2]$ was also formed, indicating the stoicheiometry in equation (1). The data in Table 2 show that low-valent or hydrido complexes of most group VIII transition metals can also be used as the catalyst component and that those of Ru, Rh, and Ir are more effective.

$$ROH + CO_2 + H_2 \longrightarrow HCO_2R + H_2O \quad (1)$$

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