

Preliminary communication

STOICHIOMETRIC INSERTION OF CARBON DIOXIDE AND ETHYLENE INTO NICKEL—CARBON BONDS

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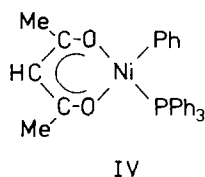
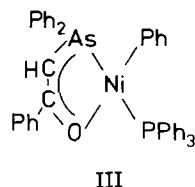
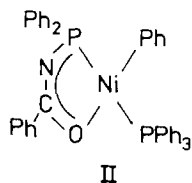
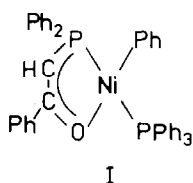
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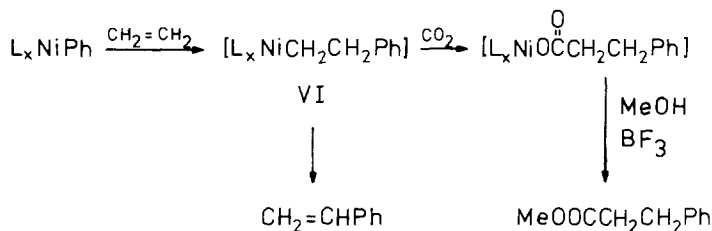
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Summary

Phenylnickel complexes containing chelate ligands react with mixtures of carbon dioxide and ethylene to yield, after esterification with methanol, hydrocinnamic acid methyl ester, methyl benzoate, styrene, ethylbenzene and n-butylbenzene.

The nickel complexes I—III are known to oligomerize ethylene to α -olefins [1—3]. A concomitant insertion of carbon dioxide could yield the corresponding carboxylic acids, a reaction, which could possibly be developed into an industrial route to the synthesis of fatty acids from ethylene and CO_2 . To gain some understanding of such a catalytic process we have studied the stoichiometric insertions of CO_2 and CO_2 /ethylene with the phenyl complexes I—IV. For zirconium [4], manganese [5], rhodium [6] and copper [7] insertions of carbon dioxide into metal—phenyl bonds have been previously reported.





Besides the co-insertion product $PhCH_2CH_2COOMe$, the products of single ethylene or carbon dioxide insertion are also observed. The co-insertion must be carried out at temperatures of about $0^\circ C$. At higher temperatures the catalytic oligomerization of ethylene predominates.

In a typical experiment, a solution of 0.44 mmol of one of the nickel ylid complexes I–III [1–3] or the related nickel acetylacetonate complex IV [9] in 15 ml toluene was transferred under argon into a 75 ml steel autoclave. After introduction of 0.2 mol carbon dioxide the solution was stirred at a temperature of $70^\circ C$ for 65 h. The co-insertion experiments were carried out with 50 mmol ethylene and 250 mmol carbon dioxide and stirred at $0^\circ C$ for 65 h. After removal of about 13 ml toluene the residue was treated with 1 ml methanol and 0.5 ml boron trifluoride etherate at $60^\circ C$ for 4 h. The solution was analyzed by GLC (Carlo Erba 2900S, WG 11 capillary column, temperature program 150 – $200^\circ C$) and GLC/MS (Varian MAT 112 S).

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