Journal of Organometallic Chemistry, 249 (1983) C38-C40 Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

Preliminary communication

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

ARNO BEHR*, WILHELM KEIM and GERHARD THELEN

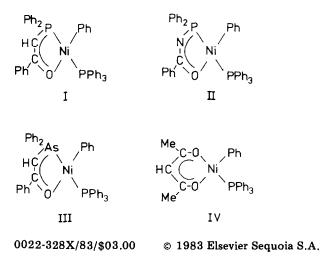
Institute of Technical Chemistry and Petrochemistry, Technical University, D-5100 Aachen (F.R. Germany)

(Received March 25th, 1983)

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 CO₂. To gain some understanding of such a catalytic process we have studied the stoichiometric insertions of CO₂ and CO₂/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.



Insertion of carbon dioxide into the nickel—phenyl bond of the complexes I to IV occurs under mild conditions. The benzoate complex V is formed as an intermediate, and this reacts with a mixture of methanol and boron trifluoride etherate to yield methyl benzoate (eq. 1).

$$L_x NiPh + CO_2 \longrightarrow [L_x NiOCPh] \xrightarrow{MeOH} PhCOOMe$$
 (1)
I-IV V

The yield of methyl benzoate, which is quite low, depends on the chelate ligand used. Some typical results are summarized in Table 1. Complex II gives the most methyl benzoate. The reactivity of the nickel—carbon bond decreases in the sequence II > III > I > IV. We assume that the low yield from complex IV is due to the influence of the two electronegative oxygen atoms in the acetylacetonate ligand. Highly basic atoms such as phosphorus and arsenic in *cis*-position to the phenyl group increase the yield of CO_2 -insertion products.

TABLE 1

INSERTION OF CO, INT	TO PHENYLNICKEL COMPLEXES	(solvent: toluene; $T 70^{\circ}C$; $t 65 h$)
-----------------------------	---------------------------	---

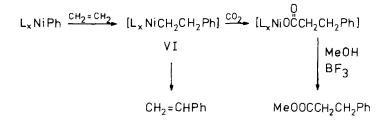
Complex	Yield of methyl benzoate (%)	
1	1.0	
п	3.3	
ш	2.6	
IV	0.5	

These results are in agreement with our observations that phenyl nickel complexes of the structure $[Ni(PPh_3)_2 XPh]$ [8] with X = Cl, Br or I in *trans*position to the phenyl group do not undergo insertion of carbon dioxide or ethylene.

In addition to the CO_2 insertion products the formation of biphenyl and acetophenone was observed. The acetophenone results from the decomposition of the ylid ligand after treatment with MeOH/BF₃.

Stoichiometric insertion of ethylene into the nickel—phenyl bond occurred with complexes I and III. Styrene (up to 1%) and ethyl benzene (1–2%) were observed. The formation of styrene can be understood in terms of insertion of one molecule ethylene to give the intermediate complex VI (eq. 2) followed by a β -elimination. Ethylbenzene can arise from VI by a hydrogen transfer. In addition, small amounts of n-butylbenzene (< 1%), identified by GLC/MS, were formed as a result of a double insertion of ethylene into the nickel phenyl bond.

Complexes I and III can also undergo co-insertion of ethylene and carbon dioxide. Mechanistically it can be assumed that in the first step one molecule of ethylene is inserted, to give the β -phenylethylnickel complex VI, and this is followed by insertion of one molecule of carbon dioxide. After esterification with MeOH/BF₃, hydrocinnamic acid methyl ester is obtained in 0.2% yield (eq. 2).



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°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°C for 65 h. The co-insertion experiments were carried out with 50 mmol ethylene and 250 mmol carbon dioxide and stirred at 0°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°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).

Acknowledgements. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- 1 W. Keim, F.H. Kowaldt, R. Goddard and C. Krüger, Angew. Chem., 90 (1978) 493; Angew. Chem. Int. Ed. Engl., 17 (1978) 466.
- 2 W. Keim, A. Behr, B. Limbäcker and C. Krüger, Angew. Chem., in press.
- 3 B. Gruber, Thesis in preparation, Technical University Aachen.
- 4 G.A. Razuvaev, L.I. Vyshinskaya, G.A. Vasil'eva, A.V. Malysheva and V.P. Mar'lin, Inorg. Chim. Acta, 44 (1980) L285.
- 5 K. Maruyama, T. Ito and A. Yamamoto, Bull. Chem. Soc. Japan, 52 (1979) 849.
- 6 I.S. Kolomnikov, A.O. Gusev, T.S. Belopotapova, M.K. Grigoryan, Y.V. Lysyak, Y.T. Struchkov and M.E. Volpin, J. Organomet. Chem., 69 (1974) C10.
- 7 G. Cahiez, J.F. Normant and D. Bernard, J. Organomet. Chem., 94 (1975) 463.
- 8 M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, J. Organomet. Chem., 30 (1971) 279.
- 9 J.M. Huggins and R.G. Bergman, J. Amer. Chem. Soc., 103 (1981) 3002.