Unusual Catalysis with Nickel(0) Complexes

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Summary Several nickel(0) complexes are excellent catalysts for the formation of alkylene carbonates from alkylene oxides and carbon dioxide.

Soluble low-valent transition metal complexes have been recognized as important agents for effecting stoicheiometric and catalytic transformations of various organic substrates. While numerous catalytic reactions have been reported involving transition-metal-activation of organic substrates containing carbon–halogen bonds,[1] carbon–carbon π-bonds,[2] and strained σ-bonds,[3] there are few data describing similar catalysis with compounds containing carbon–oxygen bonds.[4]

We report that a series of co-ordinatively unsaturated zerovalent nickel complexes catalyse the formation of alkylene carbonates‡ from certain epoxides and carbon dioxide. When epoxyethane and carbon dioxide are heated at 100° in benzene solution containing L_2Ni[5] ($L = Ph_3P$),

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‡ All inorganic complexes were satisfactorily characterized by elemental analyses, molecular wieght determinations, and i.r. and n.m.r. spectroscopy while the organic carbonates gave mass, i.r., and n.m.r. spectra consistent with their structures.

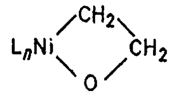
TABLE

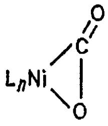
Preparation of alkylene carbonates catalysed by Ni^0 *complexes*[a]

Catalyst[b] *(0·25 g)*	Reactants[c]	Time (t/h)	Epoxide conversion (%)	Products
(A)	Epoxyethane	4	25	Ethylene carbonate[d]
(A)	,,	12	50	,, [d]
(B)	,,	4	60	,, [d]
(C)	,,	24	25	,, [d]
(D)[e]	,,	24	*ca.* 1	,,
(B)	2-Methyl-1,2-epoxypropane	48	*ca.* 100	1,1-Dimethylethylene carbonate[d]
(C)	,,	48	*ca.* 25	,,
(B)	2,3-Epoxybutane	24	*ca.* 1	1,2-Dimethylethylene carbonate
(A)	1-Chloro-2,3-epoxypropane	10	100	Chloromethylethylene carbonate[d]
(E)	,,	10	75	,, [g]

[a] Reactions were run in 80 ml stainless steel autoclaves with rigorous exclusion of moisture and air in 15 ml of C_6H_6 at 100°. [b] (A): $(Ph_3P)_2Ni$; (B): $[(C_6H_{11})_3P]_2Ni$; (C): $(C_6H_{11})_3P$; (D): (cyclo-octadiene)$_2$Ni; (E): Ph_3P. [c] 15 ml reactant charged with 500 psi gauge CO_2 pressure throughout. [d] > 95% selectivity. [e] 0·11 g catalyst. [f] *Ca.* 70% selectivity. [g] 70% selectivity.

ethylene carbonate is formed in >95% selectivity. Under similar conditions (see Table) 2-methyl-1,2-epoxypropane and 1-chloro-2,3-epoxypropane are converted into their corresponding carbonates in good yields while 2,3-epoxybutane (*cis*- and *trans*-mixture) is converted slowly into the corresponding carbonate.


(I)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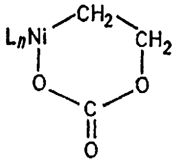
(III)

Control experiments demonstrated that Ph_3P or $Ph_3P{=}O$ are not catalysts for the preparation of ethylene carbonate under simulated reaction conditions. Triphenylphosphine does catalyse carbonate formation from 1-chloro-2,3-epoxypropane and similarly tricyclohexylphosphine yields carbonate from 2-methyl-1,2-epoxypropane, but at appreciably slower rates and reduced selectivities than their derived nickel complexes.

The rate of alkylene carbonate formation is dependent on the structure of the epoxide and catalyst; it decreases in the order $H_2\overline{C\cdot O\cdot C}H\cdot CH_2Cl > H_2\overline{C\cdot O\cdot C}H_2 > Me_2\overline{C\cdot O\cdot C}H_2 > MeH\overline{C\cdot O\cdot C}HMe$ and $[(\mathrm{cyclohexyl})_3P]_2Ni > (Ph_3P)_2Ni > (\mathrm{cyclohexyl})_3P > (\mathrm{cyclo\text{-}octadiene})_2Ni > Ph_3P$. This suggests that the catalyst, behaving as a nucleophile, directly or indirectly induces epoxide ring opening. This interpretation resembles the reported[6] base-catalysed formation of alkylene carbonates from epoxides and carbon dioxide.

The catalytic scheme may be viewed as a repeating sequence of oxidative addition, insertion, and reductive elimination steps involving intermediates such as (I) and/or (II)[7] and (III). Various L_2Ni complexes proved to be useful catalysts in other nucleophile-promoted reactions,[8] *e.g.*, the trimerization of methyl isocyanate to the isocyanurate and the dimerization of keten dimer.

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[1] G. P. Chuisoli and L. Cassar, *Angew. Chem. Internat. Edn.*, 1967, **6**, 124.

[2] (a) P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1970, **8**, 48; (b) G. C. Bailey, *Catalysis Rev.*, 1969, **3**, 37.

[3] J. P. Candlin, A. W. Parkins, and K. A. Taylor, *Ann. Reports*, 1970, **67B**, 314.

[4] *E.g.*, transition-metal catalysis with aldehydes and ketones, see ref. 2a, p. 39; for transition-metal epoxide activation see E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, 1967, **89**, 2755; A. J. Chalk, *Chem. Comm.*, 1970, 847; S. Fukuoka, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1970, **35**, 3184.

[5] The nickel(0) complexes were prepared by the sodium amalgam reduction of the corresponding bis-tertiary-phosphinenickel dihalide complexes; see *e.g.* R. J. De Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.

[6] P. P. McClellan, U.S.P. 1959, 2,873,282 (*Chem. Abs.*, 1959, 15987i); A. L. Shapiro, S. Z. Levin, and V. P. Chekhovskaya, *Zhur. org. Khim.*, 1968, **4**, 2065, and references cited therein.

[7] Similar transition-metal–carbon dioxide complexes have been isolated; see *e.g.* P. W. Jolly, K. Jonas, C. Krüger, and Y. H. Tsay, *J. Organometallic Chem.*, 1971, **33**, 109; G. G. Aleksandrov, Yu. T. Struckhov, and M. E. Vol'pin, *Chem. Comm.*, 1971, 972. Intermediates (I)—(III) might be zwitterions.

[8] H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York, London, 1967.