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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

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substrates containing carbon-halogen bonds,¹ carboncarbon 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 = Ph₃P),

‡ 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	complexesa

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Reactants ^c	Time (t/h)	Epoxide conversion (%)	$\operatorname{Prod}\operatorname{ucts}$
Epoxyethane	4	25	Ethylene carbonated
1 <i>,</i> ,	12	50	,, d
	4	60	d
	24	25	,, d
22	24	ca. 1	
2-Methyl-1,2-epoxypropane	48	ca. 100	1,1-Dimethylethylene carbonated
,,	48	ca. 25	
2,3-Epoxybutane	24	ca. 1	1,2-Dimethylethylene carbonate
1-Chloro-2,3-epoxypropane	10	100	Chloromethylethylene carbonated
,,	10	75	,, g
	Reactants ^e Epoxyethane 	ReactantseTime (t/h) Epoxyethane4,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Reactantse Time (t/h) Epoxide (t/h) Epoxyethane 4 25 "," 12 50 "," 24 25 "," 24 25 "," 24 25 "," 24 25 "," 4 60 "," 24 25 "," 24 25 "," 24 25 "," 24 25 "," 24 25 "," 24 25 "," 24 25 "," 148 ca. 1 2-Methyl-1,2-epoxypropane 48 ca. 25 2,3-Epoxybutane 24 ca. 1 1-Chloro-2,3-epoxypropane 10 100 "," 10 75

^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): (Ph₃P)₂Ni; (B): $[(C_6H_{11})_3P]_2$ Ni; (C): $(C_6H_{11})_3$ P; (D): (cyclo-octadiene)₂Ni; (E): Ph₃P. ° 15 ml reactant charged with 500 psi gauge CO₂ 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.



Control experiments demonstrated that Ph₂P or Ph₃P=O are not catalysts for the preparation of ethylene carbonate under simulated reaction conditions. Triphenylphosphine does catalyse carbonate formation from 1-chloro-2,3epoxypropane and similarly tricyclohexylphosphine yields carbonate from 2-methyl-1,2-epoxypropane, but at appreciably slower rates and reduced selectivities than their derived nickel complexes.

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.

* 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.

⁶ 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.

Similar transition-metal-carbon dioxide complexes have been isolated; see e.g. P. W. Jolly, K. Jonas, C. Krüger, and Y. H. Tsay, . 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.

The rate of alkylene carbonate formation is dependent on the structure of the epoxide and catalyst; it decreases in the

$$\text{order } H_2\dot{C} \cdot \dot{O} \cdot \dot{C}H \cdot CH_2Cl > H_2\dot{C} \cdot \dot{O} \cdot \dot{C}H_2 > Me_2\dot{C} \cdot \dot{O} \cdot \dot{C}H_2$$

> MeHC·O·CHMe and $[(cyclohexyl)_3P]_2Ni > (Ph_3P)_2Ni >$ $(cyclohexyl)_{3}P > (cyclo-octadiene)_{2}Ni > Ph_{3}P$. This suggests that the catalyst, behaving as a nucleophile, directly or indirectly induces epoxide ring opening. This interpretation resembles the reported⁶ 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 L₂Ni 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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