

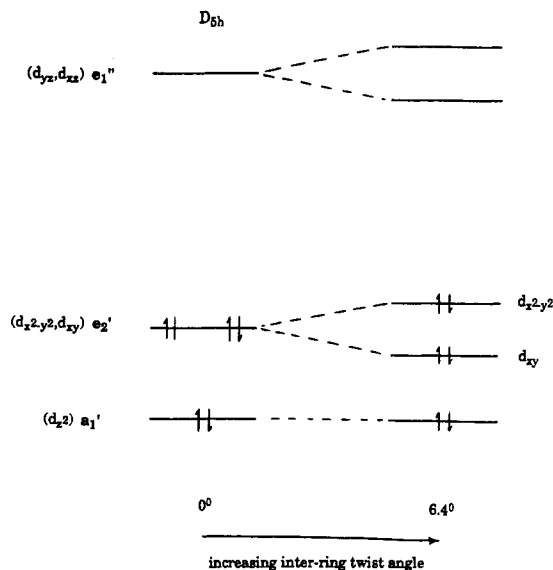


Figure 8. Schematic molecular orbital energy level diagram showing the lifting of metal-centered orbital degeneracies as the inter-ring twist angle increases, thereby lowering the metallocene symmetry from eclipsed (local D_{5h}).

what for C-4' and C-5', (again treatment of the $d_{x^2-y^2}$ orbital interactions yields the reverse orderings.) Therefore the extent of the d_{xy} -ligand interactions in 1 and 2 (assuming the two are isostructural) places electron density in the vicinity of the ^{13}C ring nuclei in the order C-1' > C-5' >>

C-2' > C-4' >> C-3'. Since this interaction is bonding, the decrease in electron density about each ^{13}C nucleus for the 4d metallocene, 2, compared with 1, which involves less diffuse 3d orbitals, would follow the same order. Therefore in 2, we expect the relative deshielding of resonances compared to those of 1 to be in the order C-1' > C-5' >> C-2' > C-4' >> C-3', and reference to Table IV indicates this to be so. However this argument holds only for consideration of the d_{xy} interaction, and for the $d_{x^2-y^2}$ interaction exactly the reverse trends are anticipated. The experimental NMR shift data may be rationalized as the consequence of twist angle which lifts the degeneracy of the e_2' energies for the exactly eclipsed (local D_{5h}) conformation, and it is the molecular orbital composed principally by the metal-centered d_{xy} orbital that becomes more strongly bonding, as illustrated in Figure 8. Therefore, comparison of the relative chemical shifts for the cyclopentadiene ring carbons for the two homologues in effect utilizes the carbon nuclei as probes for the distribution of electron density within the metallocene framework, which is seen to increase for symmetries lower than D_{5h} in accord with the symmetry associated with the metal-centered d_{xy} orbital.

Acknowledgment. We thank Fran Gallwey for collection of the NMR data and RTZ Chemicals Ltd. for financial support (N.W.S.). We also wish to acknowledge a gift of ruthenium chloride from Johnson Matthey Ltd., which was the source of compound 2.¹⁸

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Electrochemical Synthesis and Structure of $\text{Sn}[\text{Co}(\text{CO})_4]_4$ and Its Use as a Stable Precursor of $[\text{Co}(\text{CO})_4]^-$ for the Catalysis of Hydrolysis of Propylene Carbonate

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The complex $\text{Sn}[\text{Co}(\text{CO})_4]_4$ (I) has been prepared in high yield by the controlled potential electrolysis of $\text{Co}_2(\text{CO})_8$ in the presence of a tin anode. The major advantage afforded by this electrochemical synthesis is to produce I quickly and cleanly. Results of an X-ray diffraction study on I are reported. We have established that I and $\text{Co}_2(\text{CO})_8$ are very active catalysts for the hydrolysis of cyclic organic carbonates. The 100% selectivity in monoglycol is in marked contrast to other catalytic systems that require an excess of water to inhibit production of polyglycols. Studies, under various CO pressures, of the catalytic activities of $\text{Co}_2(\text{CO})_8$ and I during the hydrolysis of propylene carbonate have led us to suggest that (i) $[\text{Co}(\text{CO})_4]^-$ is the active moiety, (ii) I can eliminate $\text{Co}_2(\text{CO})_8$, and (iii) I is more stable than $\text{Co}_2(\text{CO})_8$ at low CO pressures. Isotopic analysis of the remaining substrate and products after the hydrolysis of propylene carbonate by H_2^{18}O show that (iv) the attack of water occurs at the carbonyl site of the carbonate and (v) it is likely that hydration is activated by $[\text{Co}(\text{CO})_4]^-$.

Introduction

We have recently reported several catalytic systems utilizing electrochemically generated catalysts.^{1,2} Electrogeneration of catalysts permits changes in the oxidation

state of the metal and gives enhanced possibility of substrate activation. We now report that the complex $\text{Sn}[\text{Co}(\text{CO})_4]_4$ (I) can be prepared in a pure state and in high yield by controlled-potential electrolysis of $\text{Co}_2(\text{CO})_8$ using

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(1) Mortreux, A.; Petit, F. *J. App. Catal.* **1986**, *24*, 1.
(2) Gilet, M.; Mortreux, A.; Folest, J. C.; Petit, F. *J. Am. Chem. Soc.* **1983**, *105*, 3876.

Table I. Atomic Coordinates and Anisotropic Thermal Parameters^d (Å²) for Sn[Co(CO)₄]₄ (I)

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Sn	0	0	0	0.0413 (7) ^a			0 ^b		
Co	0.08911 (8)	-0.08911	0.08911	0.0523 (8) ^a			0.0044 (8) ^c		
C(1)	0.0081 (8)	-0.1007 (8)	0.1507 (7)	0.046 (7)	0.073 (8)	0.073 (8)	0.002 (8)	-0.031 (8)	0.003 (8)
C(2)	0.1499 (9)	-0.1499	0.1499	0.091 (7) ^a			0.000 (10) ^c		
O(1)	-0.0425 (5)	-0.1084 (6)	0.1938 (5)	0.071 (6)	0.137 (10)	0.068 (6)	0.017 (7)	0.024 (6)	-0.004 (7)
O(2)	0.1875 (6)	-0.1875	0.1875	0.138 (8) ^a			0.048 (7) ^c		

^a $U_{11} = U_{22} = U_{33}$. ^b $U_{ij} = 0$ if $i \neq j$. ^c $U_{23} = U_{12} = -U_{13}$. ^d Anisotropic temperature factor defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^{*}c^{*}kl + 2U_{13}a^{*}c^{*}hl + 2U_{12}a^{*}b^{*}hk)]$.

Table II. Bond Distances (Å) and Interbond Angles^a (deg) in Sn[Co(CO)₄]₄ (I)

Sn-Co	2.6703 (14)	Sn-Co-C(1)	87.5 (4)
Co-C(1)	1.772 (13)	Co-C(1)-O(1)	176.8 (12)
Co-C(2)	1.821 (16)	C(1)-Co-C(2)	92.6 (7)
C(1)-O(1)	1.158 (16)		
C(2)-O(2)	1.126 (19)		

^a The following angles are crystallographically imposed: Co-Sn-Co', 109.47°; Sn-Co-C(2), 180°; Co-C(2)-O(2), 180°; C(1)-Co-C(1'), 120°.

a tin anode. This complex is a remarkably active catalyst in, for example, the hydrolysis of cyclic organic carbonates.³

Results

Electroreduction of Co₂(CO)₈. The electrochemical synthesis of I offers numerous advantages over conventional chemical methods employing Sn,⁴ SnCl₂,⁵ SnAr₂,⁶ SnCl₄,⁷ and Co₂(CO)₈. Although it is based on the same principle of chemical reaction of Co₂(CO)₈ and tin, it permits a considerable increase in the rate of production of I. Moreover, the reaction of Co₂(CO)₈ and SnCl₂ gives good yields of I, but the crude product must be thoroughly purified before it shows any catalytic activity with respect to organic carbonates hydrolysis.

Electrogeneration of I. The electroreduction of Co₂(CO)₈ is performed in an undivided cell, monitored with a three-electrode system consisting of a cylindrical Sn anode, a Pt gauze cathode, and a reference electrode. The cell is charged with Co₂(CO)₈ and solvent (propylene carbonate/benzene mixture or isopropyl alcohol), and a potential of -0.8 V vs Ag/AgCl is imposed.⁸ The initial light brown color changes slowly to dark red, and a precipitate is formed. Electrolysis is continued until 1 F/mol of Co₂(CO)₈ has passed, at which time the solution has turned green. The precipitate is dried in vacuo to afford up to 60% of I. The utilization of the more volatile isopropyl alcohol as solvent enables the yield of I to be improved by evaporation.

Analysis and Structure of I. Electron microprobe experiments show that the atomic ratios Co/Sn and CO/Co are homogeneous in the precipitate and very close to 4 (3.98 (0.06)) and 4 (4.28 (1.13)). The crude product has also been identified spectroscopically (MS, IR) and has been found to be free of Co₂(CO)₈ (IR).

The molecular structure of I was established by a single-crystal X-ray diffraction study and is shown in Figure 1. Table I lists the atomic parameters determined, and

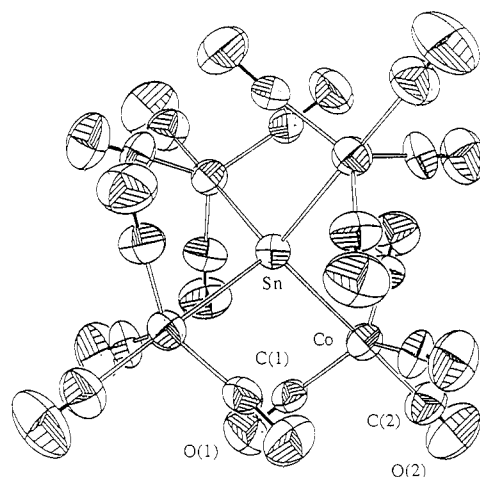
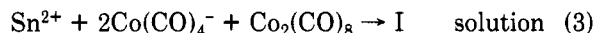
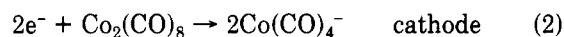
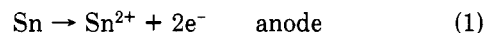
**Figure 1.** ORTEP drawing of I.

Table II hosts internuclear distances and interbond angles derived.

The molecule consists of a tetrahedral tin atom (this symmetry is crystallographically imposed⁹) covalently bonded to four [Co(CO)₄] fragments, Sn-Co 2.6703 (14) Å. The geometry about each Co is approximately C_{3v} (of which C₃ is crystallographically imposed), and, including the tin atom, the cobalt coordination is essentially trigonal bipyramidal. The equatorial carbonyl groups [C(1)O(1)] appear to be slightly inclined toward tin [C(1)-Co-Sn 87.5 (4)°, C(1)-Co-C(2) 92.6 (7)°] and more strongly bound to Co than is the axial carbonyl C(2)O(2).

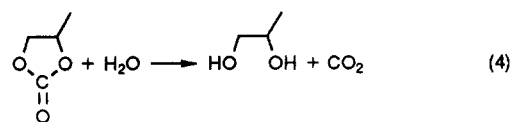
Discussion

The quantity of tin consumed from the anode together with the quantity of charge passed indicates the production of I is in accordance with eqs 1-3.



The hypothetical intermediate complex Sn[Co(CO)₄]₂ has not been detected by infrared studies, indicating that eq 3 proceeds rapidly.

Results and Discussion of the Catalytic Activity of Co₂(CO)₈ and I during Propylene Carbonate Hydrolysis. During these studies, we have also found that I and Co₂(CO)₈ are remarkably active catalysts in the hydrolysis of propylene carbonate (4-methyl-1,3-dioxolan-2-one, eq 4).



(3) Cabrera, A. Thesis, University of Lille, 1986.

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(6) Corwell, A. B.; Harrison, P. G.; Richards, J. A. *J. Organomet. Chem.* **1976**, 108, 47.

(7) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1968**, 7, 771.

(8) Cyclic voltammetry experiments on Co₂(CO)₈ in this solvent have shown a reductive half-wave potential at -0.7 V vs Ag/AgCl, which is roughly in accordance with that observed in CH₂Cl₂ by Dessy et al.: Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, 88, 5117.

(9) Bigorgne, M. *Compt. Rend.* **1968**, 266, 695.

Table III

catalyst	mol %	conversion, %	selectivity in 1,2-propanediol, %
none		0	
$\text{Co}_2(\text{CO})_8$	0.05	90 ^a	100
I	0.05	100 ^b	100
$\text{SnCl}_2 + \text{CoBr}_2$	0.05 ^c	<5	nd ^d

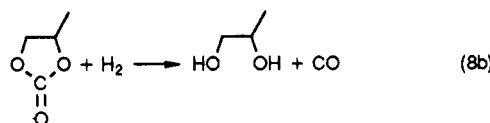
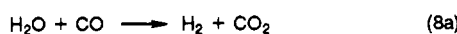
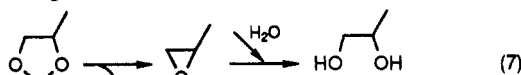
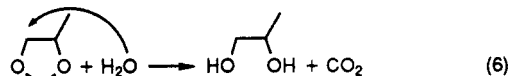
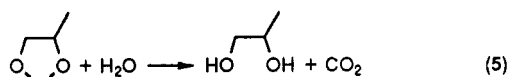
^{a,b} The best conversions rates are obtained when carbon monoxide pressures are 30 (a) and 7.5 (b) bars, found respectively at 260 and 390 h⁻¹. ^c 0.05 mol % of each salt. ^d Not determined.

Typical experiments were conducted at 150 °C in a pressurized Teflon-coated reactor, using the molar ratio [carbonate]:[H₂O] = 1:1, over 16 h. Carbon monoxide pressure is required to stabilize the catalysts.

Table III compares the reaction rates and selectivities obtained with $\text{Co}_2(\text{CO})_8$ and I.

The remarkable 100% selectivity found for $\text{Co}_2(\text{CO})_8$ and I is in marked contrast to other catalytic systems (e.g., K_2CO_3) that require an excess of H₂O to inhibit the production of polyglycol.¹⁰

General Mechanism. There are four possible pathways for this reaction: attack by water at the carbonyl (eq 5) or alkoxy (eq 6) carbons of propylene carbonate itself or at an epoxide produced by a prior decarboxylation of the carbonate (eq 7) or reduction by CO of H₂O into H₂ followed by a reduction of propylene carbonate by H₂ (eq 8).



Whatever the catalyst used, no reaction is detected when propylene carbonate is heated at 150 °C under various CO/H₂ pressures (eq 8b). Hence eq 8 has been rejected.

To choose between eq 5, 6, or 7, mass spectrometric analyses of the products of the reaction of H₂¹⁸O with natural propylene carbonate catalyzed by $\text{Co}_2(\text{CO})_8$ or I have been performed. They show the labeled oxygen to be present only in the CO₂ released. Thus water attacks only at the carbonyl site (eq 5).

Catalytic Moiety. To activate such an electrophilic site, we suggest that $\text{Co}_2(\text{CO})_8$ and I are able to produce the nucleophilic moieties $\text{Co}(\text{CO})_4^-$. Figure 2 compares catalytic behaviors of $\text{Co}_2(\text{CO})_8$ and I under various CO pressures.

The pressure dependence of the activity of $\text{Co}_2(\text{CO})_8$ under CO pressures greater than 30 bars is in accord with

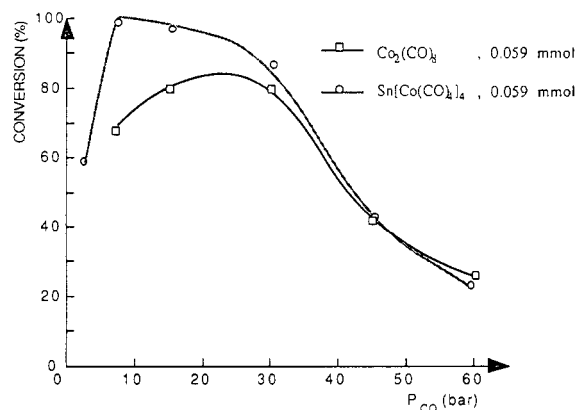


Figure 2. Propylene carbonate conversion (percent) as a function of CO pressure (bar): $T = 150\text{ }^\circ\text{C}$, $t = 16\text{ h}$; propylene carbonate, 10 mL; benzene, 15 mL; water, 2.2 mL.

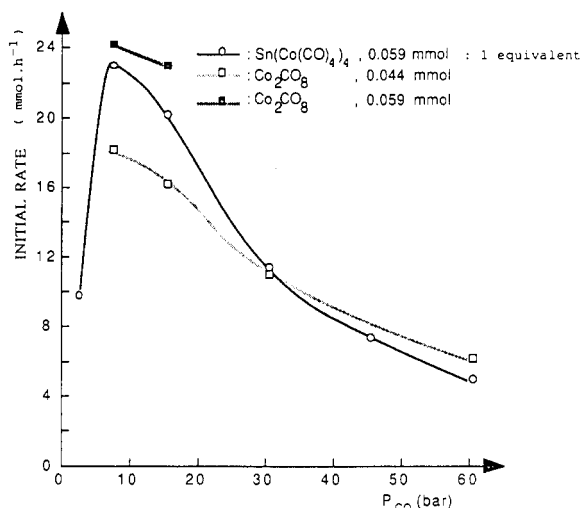
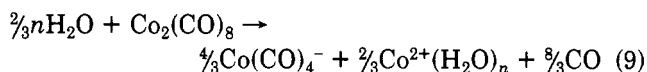
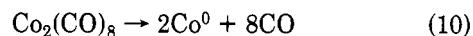


Figure 3. Initial rate (mol h^{-1}) of propylene carbonate hydrolysis as a function of CO pressure (bar): $T = 150\text{ }^\circ\text{C}$, $t = 16\text{ h}$; propylene carbonate, 10 mL; benzene 15 mL; water, 2.2 mL.

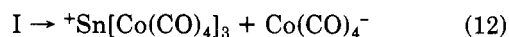
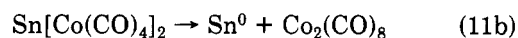
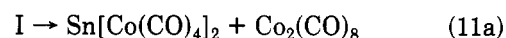
the equilibrium^{11,12} in eq 9, which is shifted to the left at high CO pressures.



At too low CO pressures ($P_{\text{CO}} = 7.5$ bars), the destruction of $\text{Co}_2(\text{CO})_8$ into metallic cobalt (eq 10) explains its lower activity.



Similarly, the activity of I is shown to have the same CO pressure dependence. This leads us to suggest that I reductively eliminates $\text{Co}_2(\text{CO})_8$ (eq 11a and 11b) rather than directly producing $\text{Co}(\text{CO})_4^-$ itself (eq 12).¹¹



(11) A pink deposit of $\text{Co}(\text{OH})_2$ can be detected in the reactor after the reaction. Experiments of hydrolysis of propylene carbonate with Co^{2+} have shown this salt does not catalyze this reaction.

(12) Fachinetti, G.; Del Cima, F.; Braca, G.; Funaioli, T. *J. Organomet. Chem.* 1984, 275, C25-C29.

Table IV

catalyst	mol %	conversion, %	selectivity, %
Li I	1	85	80 ^a
Co ₂ (CO) ₈	1	100	100
I	1	100	100

^a Acetone byproduct.

If we assume that $\text{Co}(\text{CO})_4^-$ produced from I (eq 11) followed by eq 9) has the same activity as that from $\text{Co}_2(\text{CO})_8$, we can deduce that at medium pressure ($P_{\text{CO}} = 30$ bars), reductive elimination of $\text{Co}_2(\text{CO})_8$ from 1 equiv of I yields 0.75 equiv of $\text{Co}_2(\text{CO})_8$ (Figure 3). However at low pressure, $\text{Co}_2(\text{CO})_8$ is consumed by dismutation (eq 9), and thus the equilibrium is shifted to produce up to 1 equiv of $\text{Co}_2(\text{CO})_8$ from 1 equiv of I.

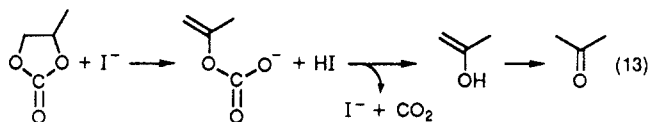
Although no deposition of metallic tin has been observed, we cannot, as yet, demonstrate that a second elimination of $\text{Co}_2(\text{CO})_8$ (eq 11b) does not occur.

Figure 2 shows that I is much more stable at low CO pressure than $\text{Co}_2(\text{CO})_8$. This might well be due to the stabilization of the eliminated $\text{Co}_2(\text{CO})_8$, which has not yet undergone dismutation, by $\text{Sn}[\text{Co}(\text{CO})_4]_2$ (eq 11a reverse).

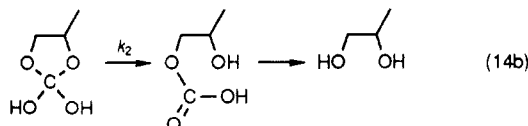
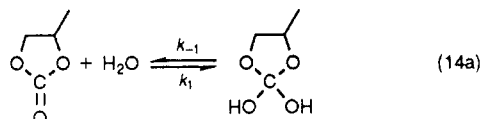
To demonstrate that $\text{Co}(\text{CO})_4^-$ reacts as a nucleophile, we have conducted experiments on the catalytic activity of the iodide anion (LiI) in our reaction conditions. Although hydrolysis occurs and the general mechanism is similar to that with $\text{Co}_2(\text{CO})_8$ or I, the rate and the selectivity are lower (Table IV).

The rate constant ratio k_{PC} (hydrolysis) (1 equiv of $\text{Co}_2(\text{CO})_8$)/ k_{PC} (hydrolysis) (1 equiv of I^-) = 40, calculated from experiments conducted under conditions of maximum dismutation of $\text{Co}_2(\text{CO})_8$, gives a good idea of the nucleophilicity of $\text{Co}(\text{CO})_4^-$.

Furthermore, the production of acetone is without doubt due to the low basicity of the iodide anion (eq 13).



Catalytic Mechanism. The propylene carbonate hydrolysis mechanism can be divided into two main steps:¹³ a hydration equilibrated process (eq 14a) followed by a ring opening (eq 14b).



Propylene carbonate hydration experiments conducted with H_2^{18}O but without any catalyst have shown this reaction occurs much more slowly ($k_1 = 1.5 \times 10^{-6} \text{ mol}^{-1} \text{ L s}^{-1}$) than the overall catalyzed reaction.

Thus we can suggest that I, $\text{Co}_2(\text{CO})_8$, and LiI catalyze at least this first step by, for example, attack of $\text{Co}(\text{CO})_4^-$ or I^- at the carbonyl group (Scheme I).

To determine if these catalysts also take part in the ring opening (eq 14b), we have compared the kinetics of hy-

Scheme I

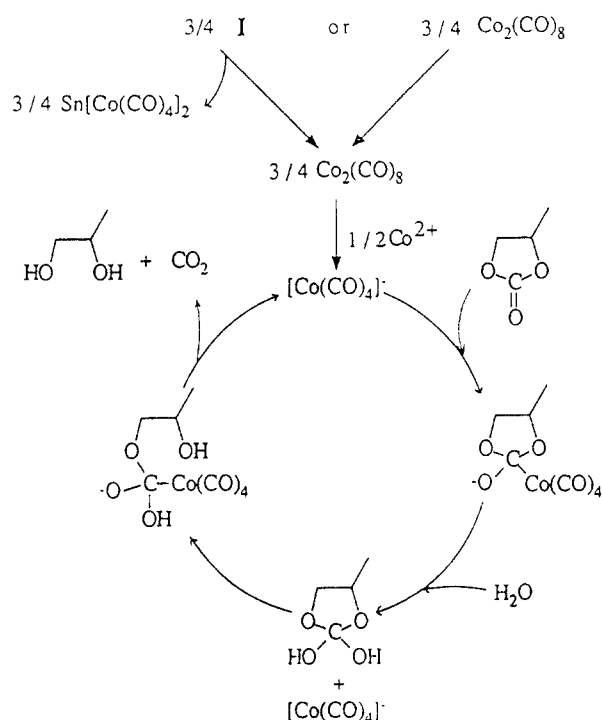


Table V

catalyst	k_2/k_{-1}
HCl	0.9
LiI	5.9
I	18

dration catalyzed by I, LiI , and HCl , because this last catalysis is supposed to happen during the hydration.

Isotopic analysis of the remaining propylene carbonate after hydrolysis with H_2^{18}O catalyzed by I, LiI , or HCl and computerized simulations of the reactions permit calculation of the ratio k_2/k_{-1} (Table V).

Conversely, we have noticed that the rate of hydrolysis is much higher when I is used than when HCl is used. Thus $k_1(\text{I}) > k_1(\text{HCl})$ and hence $k_{-1}(\text{I}) > k_{-1}(\text{HCl})$ because values of energies of the carbonate and the hydrate are independent of the nature of the catalyst.

From this and from the results displayed in Table V, we can deduce that $k_2(\text{I}) \gg k_2(\text{HCl})$.

Irrespective of whether or not HCl catalyzed the ring opening, we can conclude that I (and to a certain extent I^-) takes part in this reaction.

Here again, we can propose, by taking note of the similarities of the results obtained with I and LiI , that this step is catalyzed by nucleophilic moieties such as $\text{Co}(\text{CO})_4^-$ and I^- (Scheme I).

Conclusion

Electroreduction of $\text{Co}_2(\text{CO})_8$ in the presence of a tin anode yields the covalent species $\text{Sn}[\text{Co}(\text{CO})_4]_4$, identified spectroscopically and by crystallographic analysis. We have shown that $\text{Co}_2(\text{CO})_8$ and $\text{Sn}[\text{Co}(\text{CO})_4]_4$ are good catalysts for propylene carbonate hydrolysis. By studying this reaction, we have been able to show the following:

$\text{Co}(\text{CO})_4^-$ catalyzes the hydrolysis of propylene carbonate by, at least, activation of the carbonyl function of the carbonate.

$\text{Sn}[\text{Co}(\text{CO})_4]_4$ can yield $\text{Co}(\text{CO})_4^-$ through reductive elimination and dismutation of $\text{Co}_2(\text{CO})_8$.

(13) Pohoryles, L. A.; Levin, I.; Sarel, S. *J. Chem. Soc., London* 1960, 3082-86.

(14) $R = [\sum \|F_o\| - \|F_c\|] / \sum \|F_o\|$.

$\text{Sn}[\text{Co}(\text{CO})_4]_4$ is much more stable than $\text{Co}_2(\text{CO})_8$ and therefore can be used at low CO pressure.

It is thus worth noting that the advantage presented by electroreduction is not to bring the oxidation state of the cobalt atom closer to -1 , since $\text{Sn}[\text{Co}(\text{CO})_4]_4$ cannot liberate directly $\text{Co}(\text{CO})_4^-$, but rather to produce a more stable complex.

Experimental Section

All manipulations were performed under oxygen-free nitrogen. Solvents were distilled under nitrogen.

Instruments: IR, Perkin-Elmer infrared spectrometer 683, 3600 data station; electron microprobe analysis, Camebax Micro (Cameca, France); local analysis, $1 \mu\text{m}^3$ (means are obtained from 30 local analyses); mass spectrometry, NERMAG R1010 B.

Preparation of $\text{Sn}[\text{Co}(\text{CO})_4]_4$. Dicobalt octacarbonyl (50.0 mg, 0.146 mmol) and 25 mL of solvent (10 mL of propylene carbonate + 15 mL of benzene or 25 mL of isopropyl alcohol) are introduced into a three-electrode cell. The auxiliary electrode is a cylindrical Sn anode (2 g, Johnson Matthey, Grade 1), the working electrode is a Pt gauze, and the reference electrode is a Ag/AgCl electrode ($\text{Ag}/\text{Ag}^+ + 0.05 \text{ M } \text{NBu}_4\text{Cl}$ in propylene carbonate). A potential of -0.8 V vs Ag/AgCl is imposed. At room temperature 14.1 C ($1 \text{ F}/\text{Co}_2(\text{CO})_8$) is passed (10 min). The precipitate is dried in vacuo to afford 35.2 mg (0.044 mmol, 60%) of I. Recrystallization from pentane is possible but not required. IR (KBr): ν_{CO} 2085, 2003 cm^{-1} , (propylene carbonate) ν_{CO} 2083, 2015 cm^{-1} . MS (heaviest fragments), $\text{SnCo}_3(\text{CO})_x$ ($x = 1-12$). Anal. Found: Co/Sn = 3.98 (0.06), CO/Co = 4.28 (0.13). Calcd: Co/Sn = 4, CO/Co = 4.

Hydrolysis of Propylene Carbonate. For the catalysts $\text{Co}_2(\text{CO})_8$ and LiI, procedure 1 has been used. For I, procedures 1 and 2 are possible and give the same results. Kinetics are followed by either pressure increase or GC analysis.

Procedure 1. Into a Teflon-coated reactor are introduced 10 mL of propylene carbonate (12 g, 0.119 mol) 2.15 mL of water (2.15 g, 0.1194 mol), and the catalyst solubilized in 15 mL of benzene. Carbon monoxide is admitted at the desired pressure. The solution is heated at 150°C and stirred for 16 h.

Procedure 2. Dicobalt octacarbonyl is electroreduced in a propylene carbonate/benzene mixture (10 mL/15 mL; see preparation of $\text{Sn}[\text{Co}(\text{CO})_4]_4$). The precipitate is solubilized by smooth heating, and the solution is introduced in a Teflon-coated reactor. Then 2.15 mL (2.15 g, 0.1194 mol) of water is added. The solution is heated at 150°C and stirred for 16 h.

Isotopic Analysis of Products. The products are injected through a GC in a mass spectrometer. Ionic currents corresponding to the masses of molecular cations are integrated from the beginning to the end of the chromatographic peak. Normalization of integrals gives the isotopic distribution of the products.

Reaction of Natural Propylene Carbonate with H_2^{18}O . The isotopic distribution of initial products are for water $\text{H}_2^{16}\text{O} = 5.54\%$, $\text{H}_2^{17}\text{O} = 3.49\%$, and $\text{H}_2^{18}\text{O} = 90.97\%$ and for benzene and propylene carbonate, natural. The reaction is conducted with our standard experimental conditions. The isotopic distributions of CO_2 , 1,2-propanediol, acetone, and the remaining propylene carbonate are analyzed. In each experiment, we have found that the 1,2-propanediol has a perfectly natural isotopic distribution. Theoretical isotopic distributions, which are calculated according to eqs 5 and 13 and a hydration-equilibrated process of CO_2 and acetone, are found to be very similar to the experimental one.

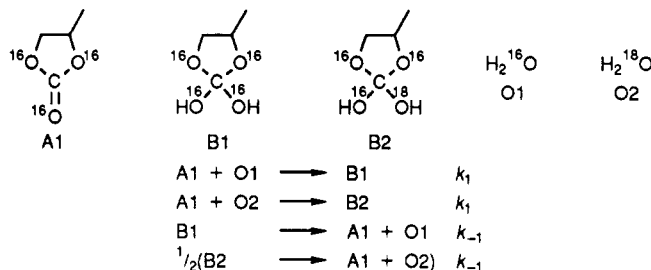
Computerized Simulation of the Hydrolysis with H_2^{18}O of Propylene Carbonate. Calculation of Rate Constants. The principle of the calculation is to find the rate constants k_1 , k_{-1} , and k_2 that give by simulation of the reaction of natural propylene carbonate with H_2^{18}O according to eq 14, the experimental final isotopic distribution of the remaining propylene carbonate. The hydration equilibrated process of CO_2 is also considered.

Table VI. Crystallographic Data for $\text{Sn}[\text{Co}(\text{CO})_4]_4$ (I)

formula	$\text{C}_{16}\text{Co}_4\text{SnO}_{16}$
mol wt	802.5
color	red
habit	equant
cryst size, mm	$0.38 \times 0.38 \times 0.40$
system	cubic
space group	$F\bar{4}3c$
temp, K	291
a , Å	17.301 (3)
V , Å ³	5178.6
Z	8
D_x , g cm ⁻³	2.058
$F(0,0,0)$	3056
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	35.29
θ range for data, deg	1.5–22.5
scan width, deg	$[2.0 + \Delta(\alpha_2 - \alpha_1)]$
total data	3820
total unique data	168
data with $I > 3\sigma(I)$	164
R^1	0.0318
no. of variables	29
max residual peak, e Å ⁻³	0.25
min residual trough, e Å ⁻³	-0.26

The number of isotopes to be considered are six for propylene carbonate, nine for the hydrate of propylene carbonate, two for water, three for 1,2-propanediol, four for CO_2 , and five for the carbonic acid.

Chemical equations are written for each isotope, i.e.



Microvariations of concentrations of isotope are calculated from kinetic equations, i.e.

$$d[\text{A1}]/dt = -k_1[\text{A1}](\text{O1} + \text{O2}) + k_{-1}[\text{B1}] + \frac{1}{2}k_{-1}[\text{B2}]$$

The concentrations at time $t + dt$ are calculated by adding the microvariation to the concentration at t , i.e.

$$[\text{A1}](t_{\text{final}}) = [\text{A1}](t = 0) + \int_0^{t_{\text{final}}} d[\text{A1}]/dt \, dt$$

Knowing every concentration at $t = 0$, numerous looping (roughly 1000) permits the calculation of concentrations at final time.

The best rate constants are found by interpolation.

Crystallographic Study. Well-formed single crystals of complex I were grown from a pentane solution of the crude product, and a suitable example was mounted on a Nicolet R3m diffractometer, operating with graphite-monochromated Mo K α radiation, $\lambda = 0.71069 \text{ Å}$. Table VI lists crystal parameters, details of intensity data collection, and information pertinent to refinement of the structure.

Data were collected by $\omega/2\theta$ scans in 96 steps at variable speeds dependent on an initial prescan and were corrected for Lorentz and polarization effects and for X-ray absorption (Ψ scans). The Sn atom is required to occupy a site of crystallographic symmetry 23. The Co atom (which lies on the crystallographic 3-fold axis) was located by analysis of the Patterson function, and the carbonyl groups by difference Fourier summations following least-squares refinement. One CO function also lies in positions (32e3) and the other lies in general space. One enantiomer (Co at $x, -x, x$) was found to afford significantly better refinement than the other (Co at x, x, x).

All atoms were refined with anisotropic thermal parameters (except that the special position of the tin atom requires it to have isotropic thermal motion), with appropriate constraints (see Table I). A number of different weighting schemes were examined, but

none gave better analysis of variance than did unit weights, which were therefore retained. Programs and packages used were SHELXTL¹⁵ on a Nova 45 minicomputer for initial structure solution, SHELX76¹⁶ on an Amdahl 470 V/8 computer for final refinement, CALC¹⁷ for molecular geometry calculations, and EASYORTEP¹⁸ for plotting. For Co, coefficients for an analytical form of the scattering curve were taken from ref 19, while inlaid¹⁶

scattering factors were used for all other atoms.

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Supplementary Material Available: Coding of the program for the computerized simulation of the hydrolysis of propylene carbonate with H₂¹⁸O (3 pages); a listing of observed and calculated structure factors for I (1 page). Ordering information is given on any current masthead page.

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Formation and Characterization of Stable Alkylidyne(alkene)tungsten Complexes

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Reaction of the alkylidyne complexes [W(CPh)Cl(CO)₂(py)₂], [Kat][W(CR)Cl₂(CO)₂(py)], and [W-(CPh)Cl(CO)₂(tmeda)] with maleic anhydride and fumaronitrile results in substitution of carbon monoxide and affords the alkylidyne(alkene)tungsten complexes [W(CPh)Cl(CO)(η^2 -alkene)(py)₂] (4 and 5), [Kat][W(CR)Cl₂(CO)(η^2 -alkene)(py)] (6 and 7; R = Me, Kat = NEt₄; 8 and 9, R = Ph, Kat = NEt₄, PPN), and [W(CPh)Cl(CO)(η^2 -alkene)(tmeda)] (10 and 11), respectively. Compounds 10 and 11 can also be obtained by reaction of 4 and 5 with tmeda. The reactions are conducted in THF or CH₂Cl₂ at room temperature or slightly elevated temperatures. In all complexes the coordination site trans to the alkylidyne ligand is occupied by chloride. ¹H NMR NOE difference studies show that in the anionic complexes the second chloride ligand is coordinated trans to the alkene. The fumaronitrile complexes are obtained as mixtures of diastereomers due to coordination of the two enantiotopic faces of the alkene to the asymmetric metal complex fragments. The molecular structure of 4 was determined by X-ray crystallography: space group P2₁/n, *a* = 11.522 (2) Å, *b* = 16.026 (3) Å, *c* = 11.680 (2) Å, β = 102.97 (1)°, *Z* = 4, *R* = 3.28%, *R*_w = 3.57%. Substitution of carbon monoxide in the formation of the title complexes is postulated to occur indirectly by initial substitution of pyridine or chloride and subsequent trans labilization of carbon monoxide by the alkene.

Introduction

Reactions of alkenes and alkynes with multiple metal-carbon bonds play a prominent role in the chemistry of transition-metal alkylidene⁴ and alkylidyne⁵ complexes. High-valent transition-metal alkylidene complexes are established as the active species in olefin metathesis⁶ and polymerization of olefins and acetylenes,⁷ and high-valent

transition-metal alkylidyne complexes are involved in acetylene metathesis.⁸ Transition-metal carbene complexes in lower formal oxidation states were found to participate in a variety of reactions.⁹ For example, they were demonstrated to be useful for the cyclopropanation of olefins¹⁰ and to generate many different organic products in reactions with acetylenes.¹¹ The Fischer-type carbyne complexes [M(CR)Br(CO)₄] were shown to induce the polymerization of certain olefins¹² and acetylenes (M = W)¹³ and to react with α,ω -diynes to form phenols (M = Cr, W).¹⁴ We have recently begun to investigate reactions of substituted Fischer-type carbyne complexes with un-

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