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$[Lewis\ Acid]^+[Co(CO)_4]^-$ Complexes: A Versatile Class of Catalysts for Carbonylative Ring Expansion of Epoxides and Aziridines**

Viswanath Mahadevan, Yutan D. Y. L. Getzler, and Geoffrey W. Coates*

Introduction of carbonyl functional groups by using transition-metal-catalyzed carbon monoxide (CO) insertion is a synthetically useful transformation.[1–3] Application of this methodology, in conjunction with readily available epoxide and aziridine substrates provides facile access to β-lactones[4] and β-lactams,[5, 6] useful precursors for organic synthesis as well as for the synthesis of polymers such as poly(3-hydroxyalkanoates)[7] and poly(β-peptides).[8, 9] Few catalysts are known to perform ring-expansive CO insertion into epoxides to give β-lactones.[10, 11, 12d] Likewise, a limited number of reagents[13] and catalysts[12, 14, 15] are known to carbonylate aziridines to yield β-lactams. Recently, regioselective epoxide and aziridine carbonylation was achieved using a catalyst system consisting of a mixture of [PPN]-$[Co(CO)_4]$ and $BF_3 \cdot Et_2O$ ($PPN = Ph_3P{=}N{=}PPh_3$).[12d] However, most of these catalysts require long reaction times, high temperatures, high catalyst loading, and/or external additives. There is continuing motivation for developing fast, single-component catalysts; ideally a single catalyst would efficiently carbonylate both epoxides and aziridines. Herein, we report a well-defined $[Cp_2Ti(thf)_2][Co(CO)_4]$ catalyst (**1**; $Cp = C_5H_5$),[16] readily synthesized from commercially available $[Cp_2Ti(CO)_2]$ and $[Co_2(CO)_8]$, is efficient for carbonylation of both epoxide and aziridine substrates. During the course of this work we discovered that the discrete catalyst [(salph)$Al(thf)_2$][$Co(CO)_4$] (**2**),[11, 17] is also active for regioselective aziridine carbonylation (Scheme 1).

The $[Co(CO)_4]^-$ ion is the putative active species for CO insertion reactions that use $[Co_2(CO)_8]$ as the catalyst.[1, 11, 12a] Based on this postulate, a variety of [cation][$Co(CO)_4$] complexes[18] were previously screened[11] for CO insertion into propylene oxide. Complexes **1** and **2** are efficient catalysts for the carbonylation of a variety of *both* epoxides and aziridines.

Catalyst **1** (5 mol %) regioselectively carbonylates a variety of epoxides under mild conditions and in high yields. Propylene oxide is converted into β-butyrolactone in 95 % yield in 4 h at 60 °C; the carbonylation is highly regioselective producing exclusively the 4-methyloxetan-2-one isomer (Table 1, entry 1). Carbonylation of propylene oxide was not observed with other potential catalysts[18, 19] under a variety of

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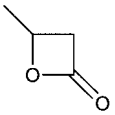
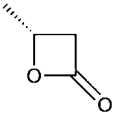
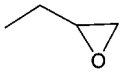
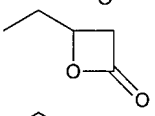
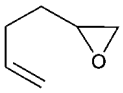
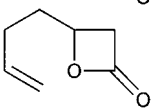
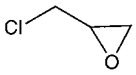
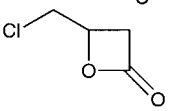
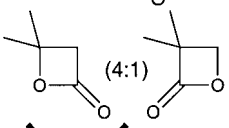
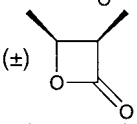
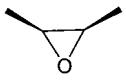
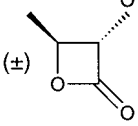
Table 1. Carbonylation of epoxides to β-lactones using **1**.[a]

Entry	Substrate	Temp [°C]	Time [h]	Products	Yield [%][b]
1		60	4		95
2		60	4		95[c]
3		60	4		99
4		60	4		90
5		60	5		60
6		50	3		90
7		60	10		99
8		60	10		75

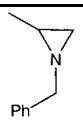
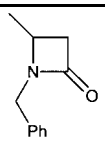
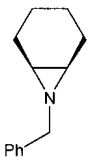
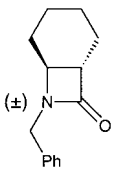
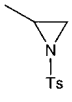
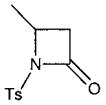
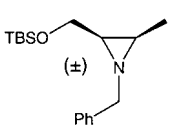
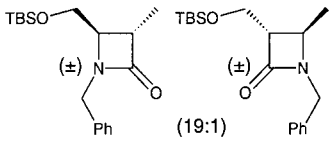
[a] 5 mol% catalyst **1** (0.2 M in DME), 6200 kPa (900 psi) CO, 1.92 mmol epoxide. [b] Yields determined by ^{1}H NMR spectroscopy. [c] >99% *(R)*-β-Butyrolactone.

conditions, which included changes in catalyst loading (2-10 mol%), temperature (50–100 °C), and reaction time (12–48 h). *(R)*-Propylene oxide is converted into *(R)*-β-butyrolactone in 95% yield with >99% retention of configuration (Table 1, entry 2), consistent with the high regioselectivity observed for CO insertion. Retention of stereochemistry allows the synthesis of enantiomerically enriched β-lactones from readily available chiral epoxides.[20] Compound **1** also catalyzes the transformation of 1,2-epoxybutane to 4-ethyloxetan-2-one (Table 1, entry 3). Functional epoxides such as 1,2-epoxy-5-hexene (Table 1, entry 4) and epichlorohydrin (Table 1, entry 5) are carbonylated to the corresponding lactones. The hindered substrate isobutylene oxide reacts to generate a mixture of isomeric lactones in a 4:1 ratio with 90% overall yield (Table 1, entry 6).

Catalyst **1** also carbonylates *cis*- and *trans*-2,3-epoxybutanes regioselectively to *trans*- and *cis*-lactones, respectively, in high yield and with inversion of configuration (Table 1, entries 7 and 8). The *cis*- and *trans*-lactone products were individually identified by comparing ^{13}C NMR spectroscopic data with those reported,[21, 22] as well as, by pyrolysis; thermal *syn* decarboxylation of the lactones generates alkenes with retention of stereochemistry.[23] Comparison of the resulting alkenes with authentic *cis*- and *trans*-2-butene samples using ^{1}H NMR spectroscopy allowed identification of the parent lactones.[24, 25]

Both **1** and **2** are capable of carbonylating aziridines to generate β-lactams, although they exhibit interesting differences in reactivity. Catalyst **1** carbonylates 1-benzyl-2-methyl aziridine in 90% yield compared to 50% obtained with **2** under similar conditions (Table 2, entry 1). However, in both cases, CO insertion occurs selectively at the least hindered ring C–N bond. Catalyst **1** also carbonylates 7-benzyl-7-azabicyclo[4.1.0]heptane in 80% yield compared to <5%

Table 2. Carbonylation of aziridines to β-lactams using **1** and **2**.[a]

Entry	Substrate	Catalyst	Temp [°C]	Time [h]	Products	Yield [%][b]
1		**1**	60	6		90
		2	60	6		50
2		**1**	80	18		80
		2	80	18		<5
3		**1**	90	6		35
		2	90	6		99
4		**1**	60	5		95

[a] 5 mol% catalyst (0.2 M in DME), 6200 kPa (900 psi) CO, 1.92 mmol aziridine; TBS = *tert*-butyldimethylsilyl, Ts = tosyl. [b] Yields determined by ^{1}H NMR spectroscopy.

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yield obtained with **2** (Table 2, entry 2). Both **1** and **2** show unprecedented activity in carbonylating the electron deficient 1-tosyl-2-methylaziridine substrate. However, **2** gives much higher lactam yields (99%) than **1** (35%) (Table 2, entry 3), which is important because of the availability of enantiomerically-pure *N*-tosyl aziridines.[26, 27] Finally, **1** reacts with *cis*-1-benzyl-2-(*tert*-butyldimethylsilyloxymethyl)-3-methyl aziridine to predominantly yield the *trans*-lactone with high selectivity for CO insertion at the (Me)C–N bond of the aziridine (Table 2, entry 4). Relative to previously reported systems, **1** and **2** react faster, under milder conditions to generate lactams in higher yield and selectivity. However, the differences in reactivity between **1** and **2** are not understood at the current time.

We propose the carbonylations of both epoxides and aziridines proceed through a unifying mechanism involving a backside nucleophilic attack by the $[Co(CO)_4]^-$ ion at the least-substituted carbon center (Scheme 1). The role of the cationic Lewis acid counterpart is to bind and activate the substrate.[11] Insertion of CO followed by ring-closure results in lactone and lactam products, with inversion of configuration at the site of attack. Discrete catalysts such as **1** and **2** will allow the elucidation of the mechanism of CO insertion into these substrates.

In summary, the discrete catalysts $[Cp_2Ti(thf)_2][Co(CO)_4]$ (**1**) and $[(salph)Al(thf)_2][Co(CO)_4]$ (**2**) are shown to efficiently carbonylate a variety of epoxides and aziridines under mild conditions. Carbonylation of (*R*)-propylene oxide can be carried efficiently on a multigram scale. Between **1** and **2**, a variety of epoxides and aziridines are efficiently carbonylated in high yield and selectivity with intriguing differences in reactivity. Further, we propose the insertion of CO into both epoxides and aziridines proceeds through a similar mechanism, which generates β-lactone and β-lactam products with inversion at the site of nucleophilic attack.

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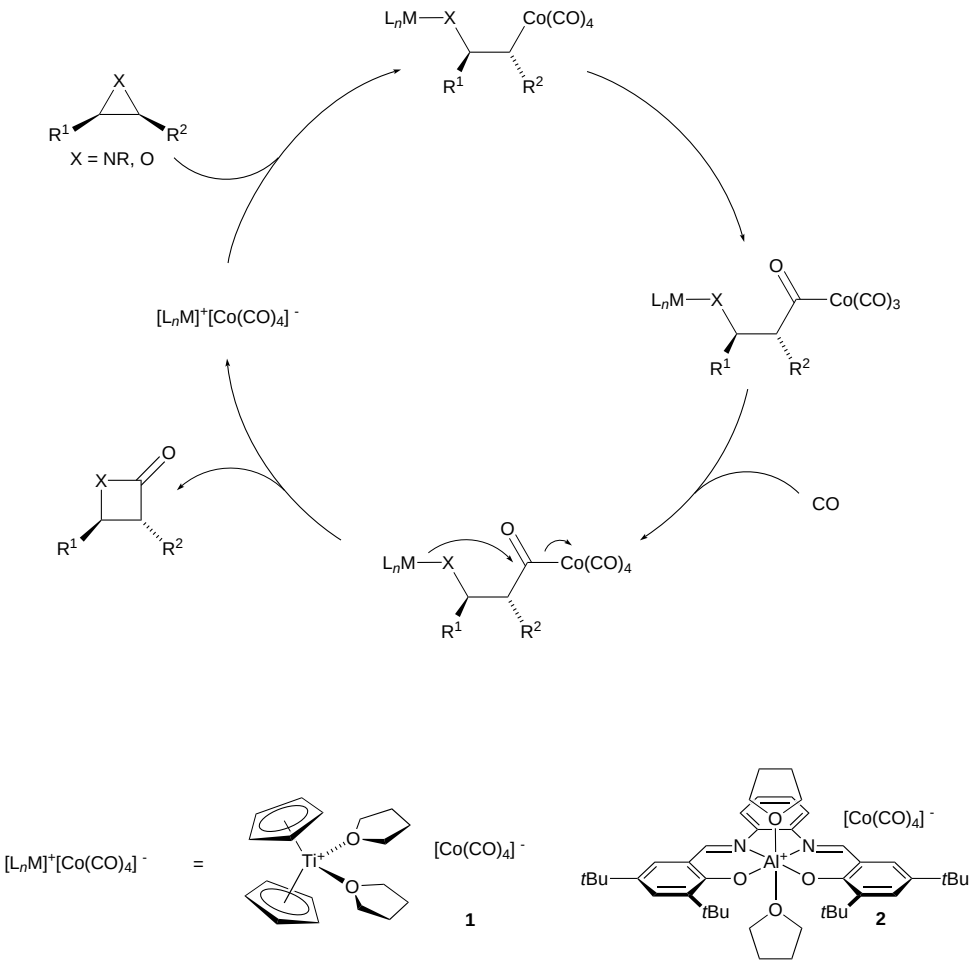

Scheme 1. Proposed catalytic cycle for epoxide and aziridine carbonylation.

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[16] Compound **1** was first synthesized by Merola and co-workers, see: a) J. S. Merola, K. S. Campo, R. A. Gentile, *Inorg. Chem.* **1989**, *28*, 2950 – 2954; b) J. S. Merola, K. S. Campo, R. A. Gentile, M. A. Modrick, *Inorg. Chim. Acta* **1989**, *165*, 87 – 90.
[17] salph = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)phenylenediamine. Catalyst **2** is highly active for epoxide carbonylation (ref. [11]).
[18] Complexes screened for activity included $Na[Co(CO)_4]$, $[Ph_4P][Co(CO)_4]$, $[nBu_4N][Co(CO)_4]$, and $[Cp_2Co][Co(CO)_4]$.
[19] During the screening phase, $Na[Co(CO)_4]$ (2 mol%, 16 h, 80 °C, 6900 kPa (1000 psi) CO, triglyme) reacted with propylene oxide to give a mixture of products, yielding mostly acetone (6%) and poly(β-hydroxybutyrate) (40%).
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[24] Alper and co-workers have reported the retention of stereochemistry in the carbonylation of 2,3-epoxybutanes (ref. [12d]), which is in variance with our results. As the result of a typographical error (personal communication, P. Dervan) in the literature upon which these assignments were based (ref. [25]), we propose that the $[PPN][Co(CO)_4]/BF_3 \cdot OEt_2$ system in fact proceeds with inversion of stereochemistry, as well.
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Remarkably High 1,5-Diastereoselectivity in a Nickel-Catalyzed Conjugate Addition of Me_2Zn and Carbonyl Compounds to 1,ω-Dienynes with Through-Space Coupling**

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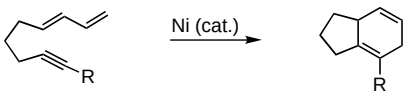
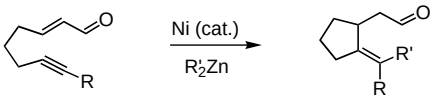
Carbon – carbon-bond formation is the most important and fundamental process in organic synthesis. In particular, the coupling reaction of unsaturated C–C bonds mediated by low-valent transition metals is a rapidly growing field and is now an indispensable strategy in synthetic chemistry.[1] Since the pioneering work of Wilke and co-workers,[2] nickel complexes have been widely utilized as efficient catalysts for C–C-bond formations.[3] Intramolecular variants such as the [4+2] cycloaddition reaction of 1,ω-dienynes [Eq. (1)],[4] cyclization of 1,ω-bis(enones),[5] ω-dienyl aldehydes,[6] and ω-alkynyl enones [Eq. (2)][7] are all useful methods for the synthesis of rather complex cyclic molecules of physiological interest.[8]



(1)



(2)

We report herein the four-component reaction of dimethylzinc, carbonyl compounds (aldehydes, ketones), and dienes and alkynes of 1,ω-dienylalkynes **1** in the presence of a catalytic amount of $[Ni(acac)_2]$ (acac = acetylacetonato) at room temperature to provide alkylidene cyclopentanes **2a**,**b** ($X = C(CO_2Et)_2$) and their heterocyclic analogues **2c**–**e** (X = O, NTs) in good yields and with excellent stereoselectivity (Table 1). This four-component reaction may be regarded as an extended version of the reactions portrayed in Equation (1) (a two-component coupling of a diene and an alkyne) and in Equation (2) (a three-component coupling of organozinc, alkyne, and enone).

The scope of the present reaction was examined with various 1,ω-dienynes **1a**–**e** (1.0 mmol) in the presence of a catalytic amount of $[Ni(acac)_2]$ (0.1 mmol), an aldehyde or ketone (2.0 mmol), and dimethylzinc (2.4 mmol) in dry THF at room temperature under nitrogen. All the 1,ω-dienynes **1a**–**e** were so reactive that almost all the reactions were complete within 1 h at room temperature, irrespective of R^1 and X of **1** and of the carbonyl compounds (Table 1). The conjugate addition of $[Me_2Zn]$ and of the carbonyl compound to 1,ω-dienynes **1** occurs at the terminal positions of the alkyne and the diene moieties, respectively; the through-space interactions of the alkyne and diene groups ensure C–C coupling at the internal positions. Terminal alkyne **1a** provided **2a** in moderate yield (Table 1, entry 1), whereas internal alkynes **1b**–**e** general gave more satisfactory results (Table 1, entries 2 – 11). Especially rewarding here is that the 1,ω-dienynes tethered by a nitrogen (**1c**) or an oxygen (**1d**,**e**) reacted with similar ease and furnished pyrrolidine and tetrahydrofuran derivatives, respectively, in reasonable yields. Bulky substituents around the carbonyl group either retard the reaction (Table 1, entry 10) or cause a decrease in yield (Table 1, entry 11). The reaction displayed a remarkably high level of stereoselectivity (> 97%, in most cases) between the cycloalkane methine and the OH-bearing carbon centers as well as excellent stereoselectivity (100%) with respect to the exocyclic tri- and tetrasubstituted double bonds.[9]

The structures of **2** were tentatively assigned by analogy with the structure of piperidine derivative **4**, which was

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