

# Reactions of early–late heterobimetallics with oxiranes: New examples for cooperative reactivity

Attila Sisak<sup>\*</sup>, Erzsébet Halmos

Research Group for Petrochemistry of the Hungarian Academy of Sciences, University of Veszprém, P.O. Box 151, H-8201 Veszprém, Hungary

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Dedicated to Professor Gyula Pályi on the occasion of his 70th birthday in recognition of his important contributions in organometallic chemistry.

## Abstract

In the reaction of oxiranes and cobalt-containing early–late heterobimetallic (ELHB) compounds isolated or prepared in situ, acyl-cobalt complexes,  $Y_3M^E OCHRCH_2C(O)Co(CO)_4$  (**1**,  $M^E = Ti, Zr, Hf$ ), were obtained. Some of the complexes **1** were isolated in form of their derivatives substituted on the cobalt atom with  $PPh_3$ . We have demonstrated that the ELHB compounds containing Group 4 metals and silyl-cobalttetracarboxyls are analogous concerning their reactivity against oxiranes. The studied heterobimetallic systems mediated the rearrangement of terminal oxiranes to ketones.

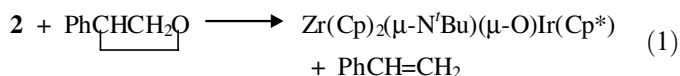
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**Keywords:** Early–late heterobimetallics; Cooperative reactivity; Oxiranes; Acyl-tetracarboxylcobalts; Ketone formation

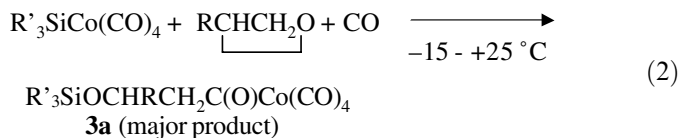
## 1. Introduction

The cooperative reactivity of early–late heterobimetallic (ELHB) complexes having a polar metal–metal bond [1–10] has been exhaustively studied in the last 15 years [1–8,10]. In general, the electropositive early metal ( $M^E$ ) centre reacts with the more Lewis basic part of the substrate, while its more Lewis acidic part will be activated by the late metal ( $M^L$ ) complex fragment [1–3]. A result of these interactions is the cleavage of the  $M^E-M^L$  single bond. Most of the substrates investigated have at least one multiple bond ( $C=O$ ,  $C\equiv N$ ,  $S=O$ , etc.) [1–3,5]. Insertion of the  $C=O$  bond – i.e. the formation of an  $M^E-O$  and an  $M^L-C$  bonds simultaneously – takes place in the cases of various carbonyl compounds [1], and the consecutive steps are strongly substrate-dependent [1,6]. Only one example exists, however, for the cooperative

activation of an oxirane, by the complex  $Zr(Cp)_2(\mu-N^tBu)Ir(Cp^*)$  (**2**); oxirane activation is accompanied by a rapid oxygen atom transfer, as shown in the following equation [1,7]:

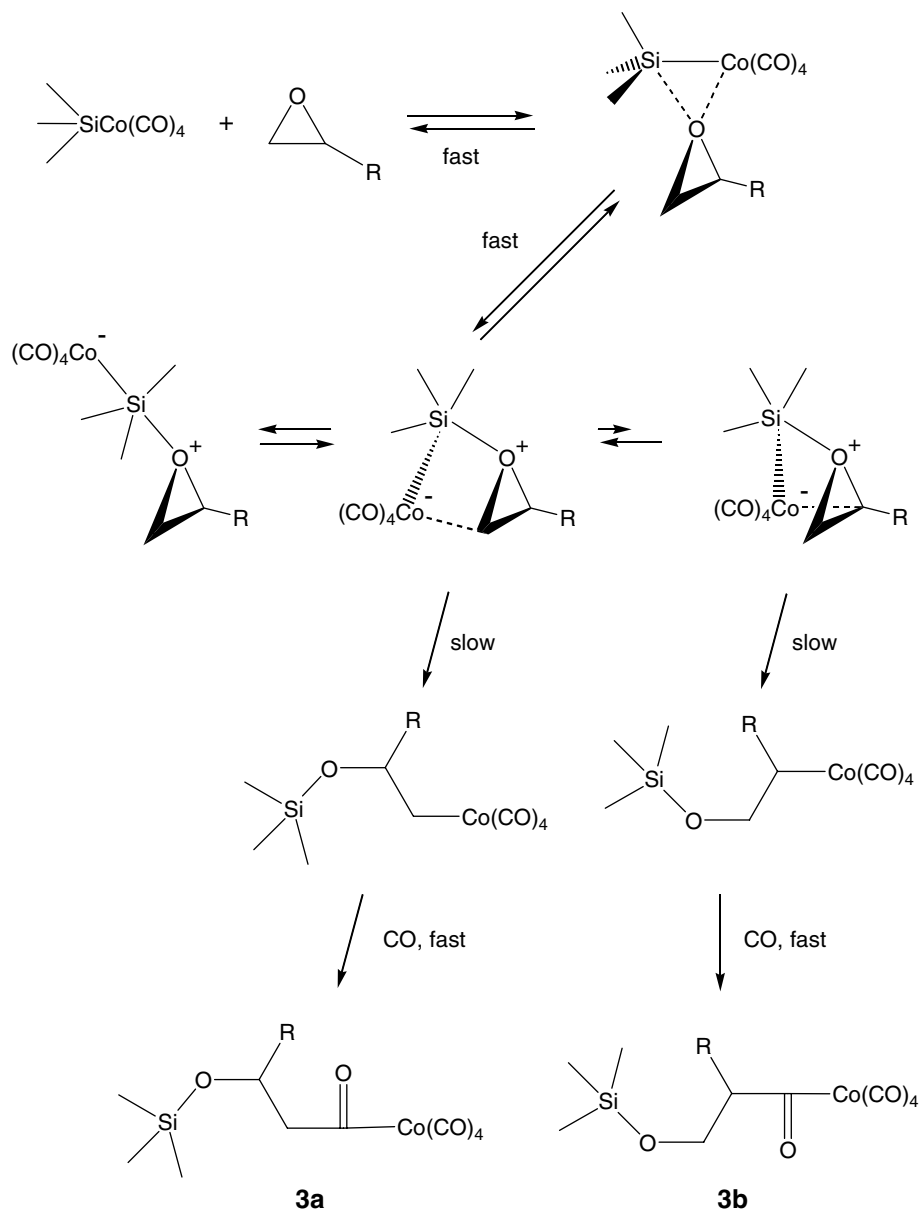


We showed earlier that terminal oxiranes react with silyl-cobalttetracarboxyls in the presence of carbon monoxide to give an isomeric mixture of ( $\beta$ -silyloxyacyl)-cobalt-tetracarboxyls (**3**) [11]:



On the basis of kinetic investigations, a mechanism involving the rapid formation of a tight ion pair, followed by a rate-determining internal  $S_N2$  type substitution, and then a fast CO insertion was suggested (Scheme 1).

<sup>\*</sup> Corresponding author. Tel.: +36 88 624718; fax: +36 88 624469.  
E-mail address: [sis014@almos.vein.hu](mailto:sis014@almos.vein.hu) (A. Sisak).



Scheme 1.

Now we report on analogous reactions starting from heterobimetallic precursors isolated or prepared in situ, as well as the transformations exhibited by the resulted acyl-cobalt complexes.

## 2. Results

The isolated ELHB complex,  $(i\text{PrO})_3\text{Ti}-\text{Co}(\text{CO})_4$  [8], reacted with methyloxirane in toluene solution under very mild conditions ( $-40$  to  $+20$  °C, Method A). The reaction was followed by IR spectroscopy, which showed an acyl-cobalttetracarbonyl as the main product (Table 1) (cf. Refs. [11–13]). Analogous complexes were formed from the following in situ prepared ELHB systems and an excess of oxiranes:

- $\text{Y}_3\text{M}^{\text{E}}\text{Cl}/\text{NaCo}(\text{CO})_4$ , at  $-40$  to  $+20$  °C in THF (Method B, cf. Ref. [9]).
- $\text{Y}_3\text{M}^{\text{E}}\text{Cl}/\text{NaCo}(\text{CO})_4$ , at  $-40$  to  $+20$  °C in toluene (Method C, cf. Refs. [8,9]).
- $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}/\text{Co}_2(\text{CO})_8$  (2:1), at  $20$  °C in toluene or dichloromethane (Method D).
- $\text{Y}_3\text{M}^{\text{E}}\text{Cl}/\text{Co}_2(\text{CO})_8/\text{Mg}$  (2:1:10), at  $0$ – $20$  °C in diethyl ether or dichloromethane (Method E).

(Y = acac, Cl, Cp,  $i\text{PrO}$ ;  $\text{M}^{\text{E}}$  = Ti, Zr, Hf, see Chart 1).

The in situ prepared ELHB systems all reacted with oxiranes to give acyl-cobalttetracarbonyls even in the absence of CO; the formation of some – partly insoluble – decomposition products and CO evolution were observed in these reactions (see later). In one case, however, the intermediate

Table 1  
Properties of the acyl-cobalt complexes **1** and **4**

Complex	Synthesis method	IR (toluene, $\nu(\text{CO})/\text{cm}^{-1}$ )	NMR ( $\text{CDCl}_3$ , $\delta$ )
<b>1a</b>	<b>A, B, C</b>	2103m, 2041s, 2021vs, 2002vs, 1717m	
<b>1b</b>	<b>B, C</b>	2103m, 2042s, 2020vs, 2001vs, 1715m	
<b>1c</b>	<b>B, D</b>	2104m, 2045m, 2122vs, 2002vs 1715m	
<b>1d</b>	<b>B, C, E</b>	2108m, 2147s, 2125vs, 2007vs, 1719m <sup>a</sup>	<sup>1</sup> H: 0.80 (3H, t, $J = 6.7$ Hz, $\text{CH}_3$ ), 1.3 (1H, m, $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 1.60 (2H, m, $\text{CH}_2\text{CH}$ ), 3.34 (1H, dd, $J = 7.3$ Hz, 11.2 Hz, $\text{CH}_a\text{H}_b\text{CO}$ ), 3.51 (1H, dd, $J = 3.8$ Hz, 11.2 Hz $\text{CH}_a\text{H}_b\text{CO}$ ), 3.86 (1H, m, $\text{CHOTi}$ ), 6.31 (10H, s, $\text{C}_5\text{H}_5$ ) <sup>b</sup> <sup>13</sup> C: 14.2 ( $\text{CH}_3$ ), 23.1 ( $\text{CH}_3\text{CH}_2$ ), 28.6 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 34.5 ( $\text{CH}_2\text{O}$ ), 67.6 ( $\text{CH}_2\text{CO}$ ), 72.0 (CH) 118.8 (Cp), 204.3 ( $\text{C}\equiv\text{O}$ ), 228.1 ( $\text{C}=\text{O}$ ) <sup>b</sup>
<b>1e</b>	<b>B, C, D, E</b>	2107m, 2145s, 2125vs, 2006vs, 1719m <sup>a</sup>	
<b>1f</b>	<b>B</b>	2106m, 2043s, 2023vs, 2003vs, 1716m <sup>c</sup>	
<b>4a</b>	<b>B, C<sup>d</sup></b>	2046w, 1978vs, 1959vs, 1680w	<sup>1</sup> H: 1.24 (18H, d, $J = 6.6$ Hz, $(\text{CH}_3)_2\text{CH}$ ), 1.36 (3H, d, $J = 7.1$ Hz, $\text{CH}_3\text{CHCH}_2$ ), 3.41 (2H, m, $\text{CH}_2\text{CO}$ ), 4.18 (1H, m, $\text{CH}_3\text{CHCH}_2$ ), 4.35 (3H, m, $(\text{CH}_3)_2\text{CH}$ ), 6.90–7.70 (m, 15H, $\text{C}_6\text{H}_5$ ) <sup>13</sup> C: 19.3 ( $\text{CH}_3\text{CH}$ ) 22.1 ( $(\text{CH}_3)_2\text{CH}$ ), 64.5 ( $(\text{CH}_3)_2\text{CH}$ ), 68.9 ( $\text{CH}_2\text{CO}$ ), 73.1 ( $\text{CH}_3\text{CH}$ ), 129.3 ( $\text{C}_m$ ), 131.5 ( $\text{C}_p$ ), 133.7 ( $\text{C}_o$ ), 135.8 ( $\text{C}_{ipso}$ ), 205.5 ( $\text{C}\equiv\text{O}$ ), 230.3 ( $\text{C}=\text{O}$ )
<b>4b</b>	<b>B, C<sup>d</sup></b>	2042w, 1977vs, 1959vs, 1685w <sup>e</sup>	<sup>1</sup> H: 1.05 (3H, d, $J = 7.3$ Hz, $\text{CH}_3$ ), 3.37 (2H, m, $\text{CH}_2\text{CO}$ ), 4.09 (1H, m, CH), 6.25 (10H, s, $\text{C}_5\text{H}_5$ ), 6.75–7.60 (15H, m, $\text{C}_6\text{H}_5$ )
<b>4c</b>	<b>C, D<sup>d</sup></b>	2044w, 1978vs, 1961vs, 1685w <sup>e</sup>	<sup>1</sup> H: 1.03 (3H, d, $J = 7.2$ Hz, $\text{CH}_3$ ), 3.34 (2H, d, $\text{CH}_2\text{CO}$ ), 4.07 (1H, m, CH), 6.22 (10H, s, $\text{C}_5\text{H}_5$ ), 6.70–7.55 (15H, m, $\text{C}_6\text{H}_5$ )

<sup>a</sup> In  $\text{Et}_2\text{O}$ .

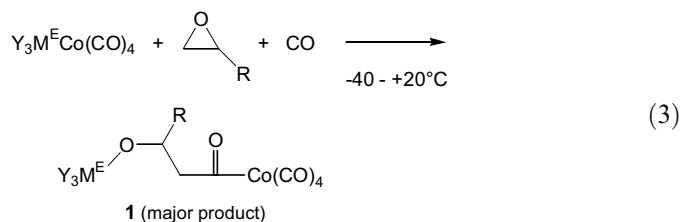
<sup>b</sup> Chemical shifts assigned to **1d** found in the reaction mixture  $(\text{Cp})_2\text{TiCl}_2/\text{Co}_2(\text{CO})_8/\text{Mg}/\text{butyloxirane}$  in  $\text{CD}_2\text{Cl}_2$  under CO (Method E, see Section 5).

<sup>c</sup> In THF.

<sup>d</sup> Synthesis methods of the precursor complex **1a–c** (see Section 5).

<sup>e</sup> In toluene:methylcyclohexane = 2:1.

alkyl-cobalttetracarbonyl could be detected as well: in the IR spectra of the system  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}/\text{Co}_2(\text{CO})_8/\text{butyloxirane}$  (Method D), the bands of both the alkyl- and acyl-cobalt carbonyls were found (Fig. 1). An acyl-cobalttetracarbonyl was detected also by <sup>1</sup>H and <sup>13</sup>C NMR spectra of the reaction mixture  $(\text{Cp})_2\text{TiCl}_2/\text{Co}_2(\text{CO})_8/\text{Mg}/\text{butyloxirane}/\text{CO}$  (Method E) (Table 1). In general, the above reactions are described by the following equation (Chart 1):



	$\text{M}^{\text{E}}$	$\text{Y}_3$	<b>R</b>
<b>1a</b>	Ti	( <sup>i</sup> PrO) <sub>3</sub>	Me
<b>1b</b>	Ti	Cl(Cp) <sub>2</sub>	Me
<b>1c</b>	Zr	Cl(Cp) <sub>2</sub>	Me
<b>1d</b>	Ti	Cl(Cp) <sub>2</sub>	Bu
<b>1e</b>	Zr	Cl(Cp) <sub>2</sub>	Bu
<b>1f</b>	Hf	(acac) <sub>3</sub>	Me

Chart 1.

Complexes  $\text{Y}_3\text{M}^{\text{E}}\text{OCHRCH}_2\text{C}(\text{O})\text{Co}(\text{CO})_4$  (**1**) could not be obtained in pure form, since most of them decomposed over the course of a few hours at 20 °C (**1f** even at 0 °C) in solution. The stability increased in the order **1f**  $\ll$  **1b**  $\approx$  **1c**  $\approx$  **1d**  $\approx$  **1e**  $<$  **1a**. Decomposition products and byproducts detected by IR spectroscopy include  $\text{Co}_2(\text{CO})_8$  (Methods A–C, under CO),  $\text{Co}_4(\text{CO})_{12}$  (Methods A–E, under Ar), and  $(\text{Cp})\text{Co}(\text{CO})_2$  (Methods A–E, during the preparation of **1b–e**). Except **1f**, the obtained acyl-cobalttetracarbonyls could be stabilized to some extent by adding triphenylphosphine to yield the monosubstituted derivatives **4** (Table 1). However, the isolated complexes **4a–c** also decomposed slowly under storage in a refrigerator. Till now no crystals suitable for an X-ray analysis could be obtained from these compounds.

In the presence of a large excess of oxirane, the intensity of the terminal  $\nu(\text{CO})$  bands of **1** slowly decreased and this was accompanied by a significant broadening and an increase in the “acyl”  $\nu(\text{CO})$  band. GC–MS analyses showed that the oxirane was converted to a ketone, namely, methylloxirane into acetone, and butyloxirane into 2-hexanone. Turnovers up to 20 could be achieved within 24 h at 20 °C.

### 3. Discussion

One of the new compounds, **1a**, was prepared starting from the ELHB complex (<sup>i</sup>PrO)<sub>3</sub>Ti–Co(CO)<sub>4</sub> (Method A).

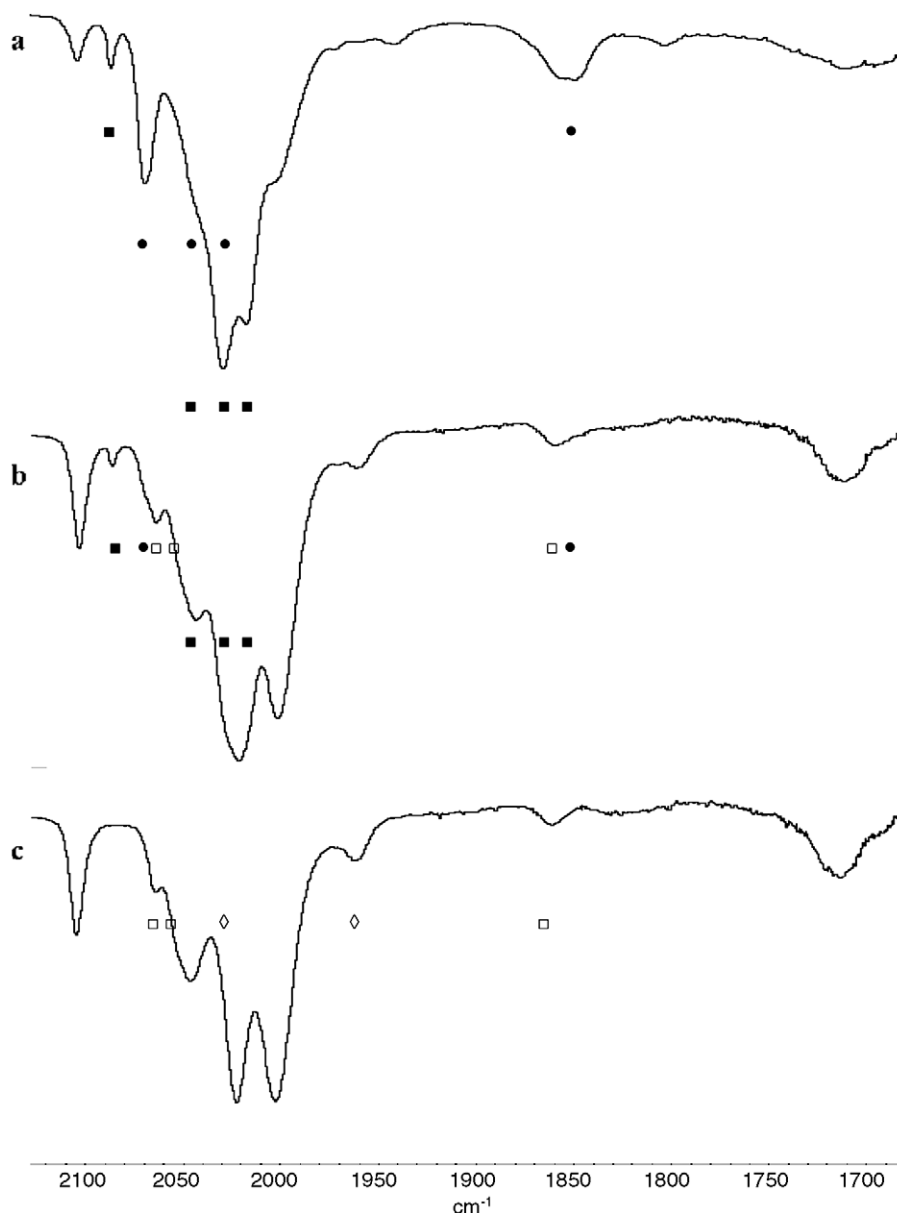


Fig. 1. IR spectra of the reaction mixture  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}/\text{Co}_2(\text{CO})_8/\text{butyloxirane}$  in the  $\nu(\text{CO})$  region (molar ratio = 2:1:3;  $[\text{Co}_2(\text{CO})_8] = 0.03 \text{ mol/l}$ ;  $20^\circ\text{C}$ ; Ar atmosphere; toluene solvent). Reaction time: 15 min (a), 150 min (b), and 240 min (c). Symbols: main product **1e** is not marked, intermediate alkyl-tetracarbonylcobalt ■,  $\text{Co}_2(\text{CO})_8$  ●,  $\text{Co}_4(\text{CO})_{12}$  □,  $(\text{Cp})\text{Co}(\text{CO})_2$  ◇.

We suppose that heterobimetallic species are the actual precursors when using Methods **B–E** as well. In the absence of the oxirane substrate, the conditions listed for Methods **B** and **C** are suitable to form a  $\text{M}^{\text{E}}\text{–Co}$  bond through the reaction of  $(^i\text{PrO})_3\text{TiCl}$  with  $\text{NaCo}(\text{CO})_4$  (see Refs. [8,9]). Till now, only heterobimetallic clusters have been obtained from the systems  $(\text{Cp})_2\text{TiCl}_2/\text{Co}_2(\text{CO})_8$  [14],  $(\text{acac})_3\text{M}^{\text{E}}\text{Cl}/\text{NaCo}(\text{CO})_4$  ( $\text{M}^{\text{E}} = \text{Zr}, \text{Hf}$ ) [5], and  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}/\text{Co}_2(\text{CO})_8$  [15]. On the other hand, a cluster containing also a Ti–Co bond,  $[(\text{CO})_9\text{Co}_3\text{CO}]_2(\text{Cp})\text{Ti–Co}(\text{CO})_4$  has been isolated from the reaction mixture of  $\text{CpTiCl}_3$  and  $\text{NaCo}(\text{CO})_4$  [16].

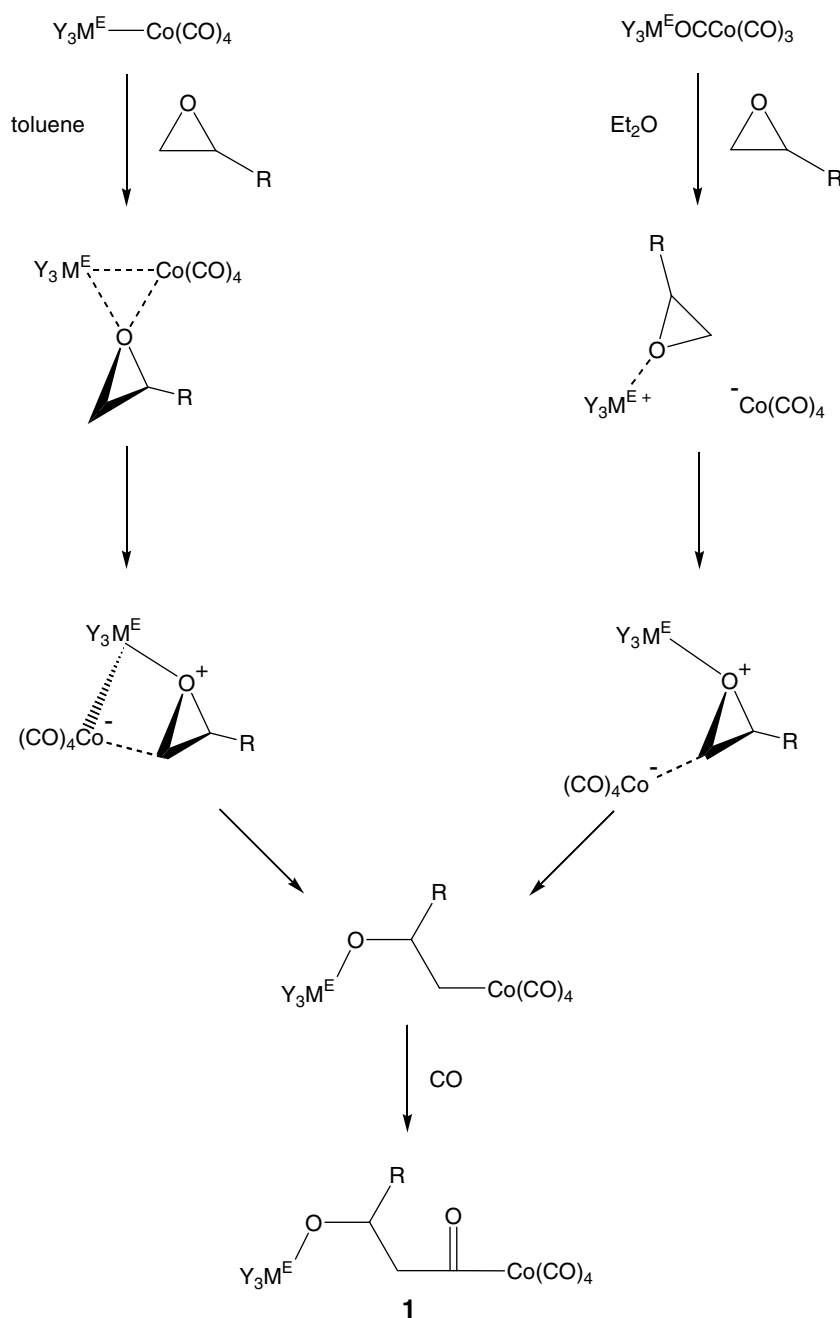
$\text{Co}_2(\text{CO})_8$  did not react with magnesium to give  $\text{Co}(-1)$  containing products in diethyl ether/oxirane (cf. conditions

of Method **E**), however, the complexes  $(\text{Cp})_2\text{M}^{\text{E}}\text{Cl}_2$  ( $\text{M}^{\text{E}} = \text{Ti}, \text{Zr}$ ) are known to transform easily into  $\text{M}^{\text{E}}(\text{III})$  species when reduced by metals like zinc or magnesium. Recently, the titanium(III) complexes,  $(\text{Cp})_2\text{TiO}^i\text{Bu}$  (**5a**) and  $(\text{Cp}^*)_2\text{TiO}^i\text{Bu}$  (**5b**), have been shown to undergo reaction with  $\text{Co}_2(\text{CO})_8$  [17]. The heterobimetallic product isolated in the case of **5b**,  $(\text{Cp}^*)_2\text{Ti}(\text{O}^i\text{Bu})(\mu\text{-OC})\text{Co}(\text{CO})_3$  (**6**), contains a titanium atom connected to cobalt by an isocarbonyl bridge. On the other hand, a metal–metal-bonded species,  $(\text{Cp})_2(\text{O}^i\text{Bu})\text{Ti–Ru}(\text{CO})_2(\text{Cp})$  (**7**) has been obtained from the photochemically induced “radical–radical” reaction of **5a** with  $[\text{CpRu}(\text{CO})_2]_2$  [18]. While the reversible dissociation of  $\text{Co}_2(\text{CO})_8$  to two  $\text{Co}(\text{CO})_4$  radicals takes place even at ambient temperature (see, e.g. Ref. [19]), a **7** type

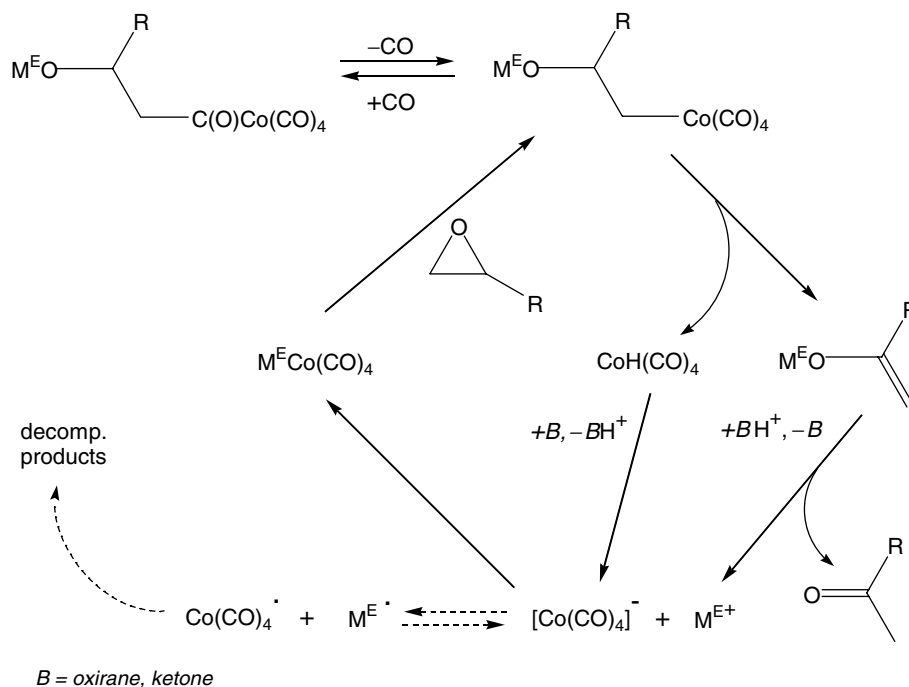
intermediate of the formation of **6** may be considered. Nevertheless, on the basis of our present experimental data, it is not possible to decide which type of precursors – **6** or **7** or both – are formed when Method E was applied.

It follows from the foregoing discussion that reaction (3) represents a new example for the cooperative reactivity of ELHB complexes. A related activation of oxiranes was described very recently using  $\text{CpRu}(\mu\text{-dppm})\text{Mn}(\text{CO})_4$ , a heterobimetallic complex with a less polar metal–metal bond [20]. The proposed pathway – supported by DFT calculations – contains the following steps: (i) the heterolytic

cleavage of the Ru–Mn bond; (ii) coordination of the oxirane oxygen atom to the Lewis acidic ruthenium centre; (iii) ring opening by the Lewis basic manganese centre. Steps (ii) and (iii) are analogous to those we proposed for reaction (2) (Scheme 1) and to those which were suggested by Coates and co-workers [13a,13b] and Allmendinger et al. [13c] for ring opening of oxiranes by  $[\text{Lewis acid}]^+ [\text{Co}(\text{CO})_4]^-$  salts. A similar mechanism may also be applied to reaction (3). Scheme 2 shows two possible routes for the formation of **1**: the precursors of acyl-cobaltracarbonyls may be metal–metal-bonded as well as an isocarbonyl-



Scheme 2.



Scheme 3.

bridged species, furthermore, both contact and isolated ion pairs may be intermediates depending on the solvent (see, e.g. Refs. [11,13,17,21,22]). A nucleophilic attack of tetracarbonyl cobaltate on the sterically more accessible carbon of the oxirane ring results in the formation of **1** through ring opening and CO insertion.

The related properties of the high oxidation state inorganic [23] and organometallic [24] compounds of Group 4 metals and Group 14 metalloids have been described several times. The consequence of reactions (2) and (3) as well as Scheme 1 and 2 is that such a relationship exists between the  $M^E$ -Co-bonded complexes containing Group 4 metals and silyl-cobalttetracarbonyls.

The rearrangement of oxiranes to carbonyl compounds catalyzed by various Lewis acids is well known [13,25]. The starting materials used in Methods A–E, however, did not catalyse such a rearrangement; moreover, a ketone was detected only when complexes **1** were also present. Consequently this rearrangement should involve ELHB compounds. In the proposed catalytic cycle outlined in Scheme 3, substituents on  $M^E$  are omitted.  $\beta$ -Hydride elimination from the alkyl complex formed by the decarbonylation of **1** produces  $HCo(CO)_4$  and the  $M^E$  enolate. The base-mediated (base = e.g. oxirane) reaction of these two species results in ketone and the ions  $M^{E+}$  and  $[Co(CO)_4]^-$ . Recombination of the latter ionic species regenerates the starting heterobimetallic complex (cf. Ref. [13]). The low turnovers achieved may be explained by the decomposition of the catalytically active species. A single-electron transfer takes place presumably from  $[Co(CO)_4]^-$  to  $M^{E+}$  leading to radicals.

## 4. Conclusions

We have found that early and late metals in the ELHB complexes of the type  $Y_3M^ECo(CO)_4$  – which may exist both in metal–metal-bonded and in isocarbonyl-bridged forms – activate oxiranes cooperatively. We have demonstrated that these ELHB compounds and silyl-tetracarbonylcobalts behave analogously since both classes of compounds react with oxiranes through a carbonylative ring-opening to give the acyl-tetracarbonylcobalt complexes,  $Y_3M^EOCHRCH_2C(O)Co(CO)_4$  and  $R'_3SiOCHRCH_2C(O)Co(CO)_4$ , respectively. This is a new example for the related reactivity of the high oxidation state Group 4 metals and Group 14 metalloids in the organometallic chemistry. The investigated ELHB systems mediated the rearrangement of oxiranes to ketones but they are less effective than certain Lewis acids.

## 5. Experimental

### 5.1. General

All manipulations involving air-sensitive compounds employed Schlenk techniques using deoxygenated, dry solvents and gases as well as reaction vessels with magnetic stirring. Infrared spectra were recorded by using a 0.04–0.12 mm  $CaF_2$  cuvette on Specord IR 75 (Carl Zeiss, Germany) or Avatar 330 FT-IR (Thermo Nicolet, USA) spectrometers, the former was calibrated with benzene ( $1959.6\text{ cm}^{-1}$ ) or polystyrene ( $1601.4\text{ cm}^{-1}$ ). The NMR measurements were performed on a Varian UNITY 300

spectrometer and a Bruker Avance 400 spectrometer. Gas chromatograms were recorded on a Hewlett–Packard model 5830 A chromatograph (with FID), while GC–MS analyses on a Hewlett–Packard 5890 Series II GC–MSD equipment using SPB1 (Supelco) capillary columns (30 m).

Materials were mainly commercial products. Oxiranes (Fluka) were dried by standard methods, distilled and stored under CO or Ar.  $(\text{Cp})_2\text{TiCl}_2$ ,  $(\text{Cp})_2\text{ZrCl}_2$ , and  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}$  were purchased from Aldrich and used without purification.  $\text{Co}_2(\text{CO})_8$  [26],  $\text{NaCo}(\text{CO})_4$  [27],  $(i\text{PrO})_3\text{TiCl}$  [28],  $(\text{acac})_3\text{HfCl}$  [29] and  $(i\text{PrO})_3\text{TiCo}(\text{CO})_4$  [8] were prepared by the literature methods.

## 5.2. Preparation of **1**

**Method A.** To  $(i\text{PrO})_3\text{TiCo}(\text{CO})_4$  (400 mg, 1.0 mmol) suspended in toluene (10 ml) at  $-40^\circ\text{C}$  under a CO atmosphere, methyloxirane (0.35 ml, 5.0 mmol) was added at once. The mixture was stirred for 30 min at this temperature and then was allowed to warm up slowly to ( $\sim 60$  min)  $20^\circ\text{C}$ . The yellow solution turned to yellow-brown. After stirring for 3 h, a probe was taken with a syringe for IR spectroscopic analysis which showed the nearly complete transformation of  $(i\text{PrO})_3\text{TiCo}(\text{CO})_4$  to an acylcobalttetracarbonyl (**1a**).

**Method B.** To a vigorously stirred solution of  $\text{NaCo}(\text{CO})_4$  (194 mg, 1.0 mmol) in THF (10 ml),  $(\text{acac})_3\text{HfCl}$  (511 mg, 1.0 mmol) was added at once under Ar at  $-40^\circ\text{C}$ . After 10 min, methyloxirane (0.35 ml, 5.0 mmol) and toluene (0.1 ml, inner standard) were injected. The reaction mixture was kept for 30 min at this temperature then was allowed to warm up slowly ( $\sim 30$  min) to  $10^\circ\text{C}$ . Meanwhile a greenish blue precipitate was separated from the brown solution. The maximum concentration of **1f** was detected by IR spectroscopy after stirring for  $\sim 40$  min at  $10^\circ\text{C}$  ( $\sim 30\%$  conversion of  $\text{NaCo}(\text{CO})_4$ ). Afterwards the intensity of the  $\nu(\text{CO})$  bands of **1f** decreased slowly except the “acyl”  $\nu(\text{CO})$  band. After 5 h reaction time, GC and GC–MS analyses of the solution showed that 46% of methyloxirane was converted to acetone.

**Method C.**  $\text{NaCo}(\text{CO})_4$  (194 mg, 1.0 mmol) and  $(\text{Cp})_2\text{ZrCl}_2$  (292 mg, 1.0 mmol) were suspended in toluene (10 ml) and stirred vigorously for 10 min under CO at  $-40^\circ\text{C}$ . Methyloxirane (0.35 ml, 5.0 mmol) was then added. The procedure was continued similarly as for Method A. The colour of the solution deepened to dark red-brown. In 3.5 h, the IR spectroscopic analysis showed the presence of **1c** as well as traces of  $\text{NaCo}(\text{CO})_4$  and  $(\text{Cp})\text{Co}(\text{CO})_2$ .

**Method D.** To  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}$  (258 mg, 1.0 mmol) suspended in the mixture of toluene (5 ml) and butyloxirane (0.36 ml, 3 mmol) under Ar at  $20^\circ\text{C}$ ,  $\text{Co}_2(\text{CO})_8$  (171 mg, 0.5 mmol) in a toluene solution (5 ml) was added at once with vigorous stirring.  $(\text{Cp})_2\text{Zr}(\text{H})\text{Cl}$  was dissolved within 30 min, while the light brown solution turned to deep red-brown. In 2 h, **1e**, the corresponding alkyl-cobalt complex, and some  $\text{Co}_2(\text{CO})_8$  were detected by IR spectroscopy. Further stirring for 2 h resulted in the complete

transformation of the alkyl intermediate to **1e**, in addition, traces of  $\text{Co}_4(\text{CO})_{12}$  and  $(\text{Cp})\text{Co}(\text{CO})_2$  were found.

**Method E.**  $\text{Co}_2(\text{CO})_8$  (342 mg, 1.0 mmol),  $(\text{Cp})_2\text{TiCl}_2$  (503 mg, 2.0 mmol), and Mg-turnings (240 mg, 10 mmol) were suspended in diethyl ether (10 ml) at  $0^\circ\text{C}$  under Ar. After stirring vigorously for 10 min, butyloxirane (0.36 ml, 3.0 mmol) was added. The mixture was allowed to warm up to  $20^\circ\text{C}$ , and stirred at this temperature for 5 h. The red-brown colour of the solution turned to green-brown and its IR spectrum showed the bands of **1d** and  $(\text{Cp})\text{Co}(\text{CO})_2$  (traces).

## 5.3. Preparation of **4**

Reaction mixtures from the preparation of **1a–c** using the above methods were filtered and evaporated at  $-20$  to  $0^\circ\text{C}$  in vacuum. The residues were dissolved in dichloromethane (5 ml) at  $0^\circ\text{C}$  under CO and triphenylphosphine (1.1 mmol/mmol of Co) was added at once with stirring. Gas evolution took place immediately. The reaction mixtures were allowed to warm up to  $20^\circ\text{C}$  and stirred for 1 h. IR spectra of the solutions showed the quantitative conversion of **1a–c** to **4a–c**. Then the solutions were filtered, hexane (0.5–1 ml) were added and the products were crystallized at  $-40^\circ\text{C}$ . The yellow-brown microcrystals were filtered, washed with  $3 \times 2$  ml of hexane and dried in vacuum.

**Compound 4a:** Yield: 34% (based on  $\text{NaCo}(\text{CO})_4$ ). Anal. Calc. for  $\text{C}_{34}\text{H}_{42}\text{O}_8\text{PTiCo}$ : C, 56.99; H, 5.91; Co, 8.22. Found: C, 57.21; H, 6.02; Co, 8.07%.

**Compound 4b:** Yield: 26% (based on  $\text{NaCo}(\text{CO})_4$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{31}\text{O}_5\text{ClPTiCo}$ : C, 59.63; H, 4.43; Co, 8.36. Found: C, 59.79; H, 4.51; 8.29%.

**Compound 4c:** Yield: 18% (based on  $\text{Co}_2(\text{CO})_8$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{31}\text{O}_5\text{ClPCoZr}$ : C, 56.18; H, 4.18; Co 7.88. Found: C, 55.98; H, 4.07, Co, 8.02%.

## 5.4. Attempt for the catalytic rearrangement of methyloxirane

To the vigorously stirred suspension of  $\text{NaCo}(\text{CO})_4$  (194 mg, 1.0 mmol) in toluene (10 ml)  $(i\text{PrO})_3\text{TiCl}$  (261 mg, 1.0 mmol) was added at once under Ar at  $-40^\circ\text{C}$ . After stirring for 10 min, methyloxirane (3.5 ml, 50 mmol) and *m*-xylene (0.5 ml, inner standard) were injected. The procedure was continued similarly as for Method A, but the mixture was stirred for 24 h at  $20^\circ\text{C}$ . GC analysis showed that 39% of methyloxirane was converted to acetone.

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