Acceptorless, Neat, Ruthenium-Catalyzed Dehydrogenative Cyclization of Diols to Lactones

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We report the dehydrogenation of 1,4-butanediol to γ-butyrolactone catalyzed by soluble ruthenium complexes without solvent or a hydrogen acceptor. An alkylphosphine version of ruthenium bis-phosphine diamine catalysts has been prepared and was found to be the longest-lived catalyst for the conversion of 1,4-butanediol to γ-butyrolactone. The catalytic production of γ-butyrolactone from 1,4-butandiol with this catalyst is simple to conduct, environmentally friendly, and highly efficient.

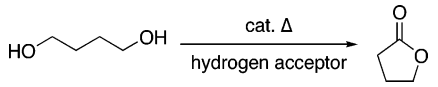
Introduction

γ-Butyrolactone is an important chemical intermediate and solvent. γ-Butyrolactone has been manufactured mainly by dehydrogenation of 1,4-butanediol with heterogeneous copper catalysts, hydrogenation of maleic anhydride, and hydrogenation of maleic esters.[1] The synthesis of γ-butyrolactone from 1,4-butanediol is particularly attractive because it does not produce any waste.[1] The hydrogen byproduct can be reused after simple purification. However, heterogeneous catalysts generally do not exhibit high selectivity for γ-butyrolactone, and tuning of the catalyst activity can be difficult. In addition, most heterogeneous catalytic cyclizations of 1,4-butanediol occur with gaseous diol. Because the reactants and the hydrogen byproduct reside in the same gas phase, it is challenging to drive the formation of γ-butyrolactone by the extrusion of hydrogen from the system.[1−3]

Many homogeneous catalysts have been developed for the dehydrogenation of diols to lactones in the presence of hydrogen acceptors.[4−6] Murahashi and co-workers reported the conversion of 1,4-butanediol to γ-butyrolactone in 99% yield with $RuH_2(PPh_3)_4$ as a catalyst and acetone as hydrogen acceptor.[4] Lin et al. reported this reaction with the iridium polyhydride $IrH_5(^iPr_3P)_2$ in 91% yield with acetone as a hydrogen acceptor.[5] Recently, Suzuki and Hiroi reported oxidative lactonization of diols with a catalyst containing an amino alcohol ligand. A variety of 1,4- or 1,5-diols were converted in this work to lactones with acetone or butanone as hydrogen acceptor. The yield of γ-butyrolactone was 96%.[6]

An oxidative cyclization suitable for large-scale production of γ-butyrolatone must occur in a neat system without a hydrogen acceptor. In contrast to the cyclizations with hydrogen acceptors, few examples of catalytic dehydrogenation of 1,4-butanediol to γ-butyrolactone have been reported without a hydrogen acceptor. Murahashi and co-workers reported that 1,4-butanediol was converted to γ-butyrolactone in the presence of $RuH_2(PPh_3)_4$ as catalyst in only 63% yield without a hydrogen acceptor.[4] Similarly, Lin et al. obtained γ-butyrolactone in only 54% yield from 1,4-butanediol without a hydrogen acceptor.[5]

Scheme 1. Catalytic Dehydrogenation with Hydrogen Acceptors



The scarcity of examples and low yields reported for acceptorless catalytic dehydrogenation of 1,4-butanediol probably results from an unfavorable equilibrium for the alcohol dehydrogenation. Because the dehydrogenation of diols to lactones is endothermic (14.7 kcal/mol),[1] it must be coupled with an exothermic reaction, such as hydrogenation of a sacrificial ketone, or conducted in an open system to obtain high yields.[1] Likewise, the dehydrogenation of alcohols to ketones and alkanes to alkenes without a hydrogen acceptor is unfavorable thermodynamically. These reactions have been reported in an open system,[7,8] but the acceptorless dehydrogenation of secondary alcohols and alkanes has been more challenging to develop than transfer hydrogenation in each case (Scheme 2).

Our strategy for the development of improved catalysts for dehydrogenation of 1,4-butanediol began with consideration of the advances in homogeneous hydrogenation of ketones during the past 20 years.[9,10] The ruthenium complexes with a diphosphine and a diamine

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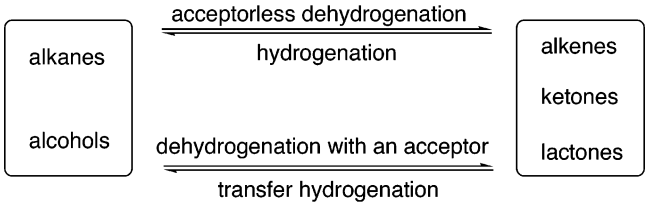
Scheme 2. Relationship between Hydrogenation and Dehydrogenation with and without an Acceptor



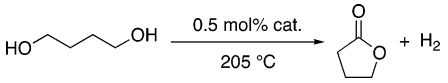
ligand introduced by Ikariya and Noyori are particularly efficient and have found wide applications.[11] These catalysts operate by a novel metal−ligand difunctional mechanism involving the transfer of hydrogen through a cyclic transition state without coordination of the ketone to the metal or generation of an alkoxide intermediate.[12] Based on microscopic reversibility, the same mechanism must be followed for the dehydrogenation of alcohols.

The most active catalysts for the forward hydrogenation reaction need not be the most active catalysts for the reverse dehydrogenation because the concentration of reagents in the two processes are different. Thus, the major transition metal complex present in the system and the turnover-limiting step may be different for the forward and reverse reactions. This difference between the activities of catalysts for reactions in the forward and reverse directions is well established in the field of enzyme kinetics.[13] Nevertheless, we thought that highly active ketone hydrogenation catalysts would be a useful starting point for the dehydrogenation of 1,4-butane diol to γ-butyrolatone. Indeed, several complexes with diphosphines and diamines reacted with rates and turnover numbers that exceed those of any previously reported system. For example, a ruthenium complex containing an aliphatic phosphine and a diamine generated the product with high conversion and selectivity and 17 500 turnovers.

Results and Discussion

Initial Catalyst Design: Catalytic Studies with Ruthenium Dihydrides. Prior to our work, Murahashi and co-workers demonstrated that $RuH_2(PPh_3)_4$ is an effective catalyst for the conversion of 1,4-butanediol to γ-butyrolactone.[4,14] Takahashi et al. at Mitsubishi Chemical Corporation reported that several ruthenium complexes prepared from $Ru(acac)_3$ and alkylphosphines under hydrogen-generated γ-butyrolactone from 1,4-butanediol in high yield without a hydrogen acceptor.[15] Because refluxing conditions are required to release dihydrogen to allow the reaction to proceed to high conversion, the reaction must be conducted at the boiling point of γ-butyrolactone, 205 °C. Thus, we set out to study ruthenium dihydride complexes with alkylphosphine ligands because alkylphosphines are more stable at high temperatures than arylphosphines.[16,17]

Table 1. Conversion of 1,4-Butanediol to γ-Butyrolactone Catalyzed by Ruthenium Dihydride and Bis-2-methylallyl Complexes[a]



entry	catalyst	time (h)	ratio (diol:GBL)[b]
1	$RuH_2(PMe_3)_4$ (**1**)	10	0:100
2	$RuH_2(PEt_3)_4$ (**2**)	10	0:97
3	$RuH_2(PBu_3)_4$ (**3**)	10	0:100
4	$RuH_2(PPh_3)_4$ (**4**)	12	19:81
5	$RuH_2(DMPE)_2$ (**5**)	10	32:57
6	$(PMe_3)_2Ru(2\text{-methylallyl})_2$ (**6a**)	10	4:93
7	$(DMPE)Ru(2\text{-methylallyl})_2$ (**6b**)	10	1:99
8	$(DIOP)Ru(2\text{-methylallyl})_2$ (**6d**)	10	9:76

[a] Reaction conditions: catalyst 0.005 mmol and 1.1 mmol of 1,4-butanediol were refluxed at 205 °C for 10−12 h in a capped vial. [b] Ratios determined by GC. When the sum of the values is less than 100%, other products were observed in the GC trace.

Table 1 summarizes our results on the catalytic dehydrogenation of 1,4-butanediol to γ-butyrolactone without a hydrogen acceptor and catalyzed by dihydride and bisallyl ruthenium complexes with alkylphosphines and several arylphosphines. Three complexes in this series (**1**, **2**, **3**) catalyzed the dehydrogenation efficiently. In contrast to the high activity of ruthenium dihydride complexes with alkylmonophosphines (**1**, **2**, **3**), $RuH_2(PPh_3)_4$ (**4**) and $RuH_2(DMPE)_2$ (**5**) (DMPE = 1,2-bis(dimethylphosphino)ethane) displayed only moderate catalytic activity for this reaction.

Catalytic Studies with Ruthenium Allyl Complexes. To test the activity of ruthenium complexes that would contain only two phosphorus donors, we synthesized several $(bisphosphine)Ru(2\text{-methylallyl})_2$ complexes (**6**) and evaluated their activity for the conversion of 1,4-butanediol to γ-butyrolactone. We anticipated that the 2-methylallyl ligand would react with the alcohol by nucleophilic attack and would be released as an allyl alcohol. Alternatively, it could react with a hydride generated by β-hydrogen elimination and would be released as an olefin. A subset of the $(bisphosphine)Ru(2\text{-methylallyl})_2$ complexes (**6**) catalyzed the dehydrogenation of 1,4-butanediol to γ-butyrolactone. Most of the complexes were only modestly reactive for this process, but $(PMe_3)_2Ru(\eta^3\text{-}(CH_2)_2CHCH_3)_2$ (**6a**) and $(DMPE)Ru(\eta^3\text{-}(CH_2)_2CHCH_3)_2$ (**6b**) were both excellent catalysts for the conversion of 1,4-butanediol to γ-butyrolactone (Table 1).

Reaction Mechanism and Identification of a Potential Mode of Catalyst Decomposition. A likely mechanism for the reaction catalyzed by Ru dihydride complexes involves an alkoxide intermediate, as shown in Scheme 4. In this mechanism, phosphine dissociation is followed by coordination of the alcohol. Proton transfer would yield a ruthenium alkoxide with a coordinated dihydrogen, and dissociation of hydrogen would generate a ruthenium alkoxide.[18] β-Hydrogen elimination

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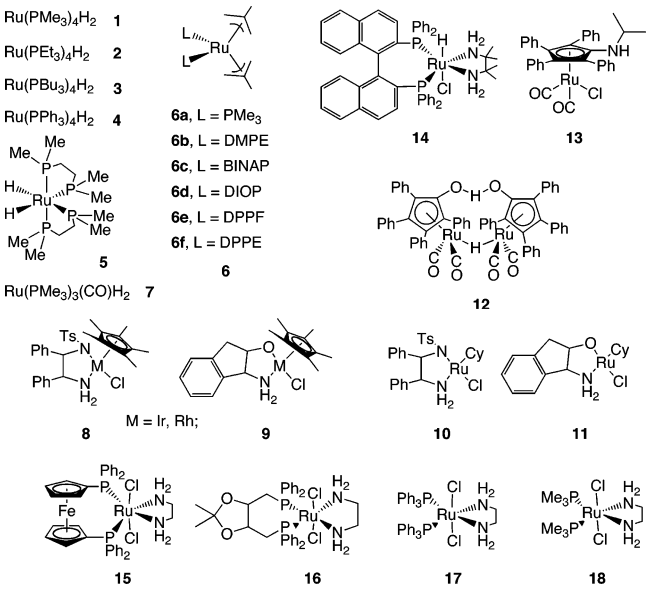
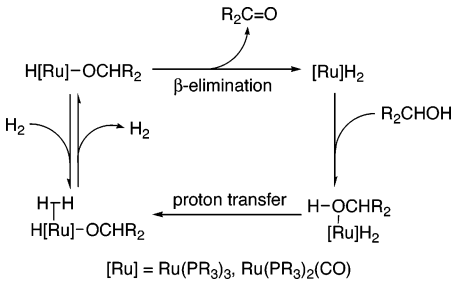
Scheme 3. Catalyst Structures



Scheme 4



from the ruthenium alkoxide would then furnish the ketone or aldehyde and the starting ruthenium dihydride.

The reaction of 1,4-butanediol at 205 °C in the presence of $RuH_2(PMe_3)_4$ as catalyst generated several ruthenium complexes. The isolation of these intermediates was complicated by the presence of neat, high-boiling γ-butyrolactone. We were unable to obtain these complexes as solids by precipitation from the solvent and were unable to isolate any of them in pure form after evaporation of the lactone at elevated temperatures.

To obtain a less soluble and more crystalline product, we conducted the dehydrogenative cyclization of 1,2-benzenedimethanol in toluene at 130 °C with 13 mol % $RuH_2(PMe_3)_4$. After 10 h, a major complex was formed, and this complex was also present in the cyclization reaction of 1,4-butanediol catalyzed by $RuH_2(PMe_3)_4$, as judged by comparison of ^{31}P NMR chemical shifts. Because 1,2-benzenedimethanol and the phthalide product of cyclization are solids, we were able to separate the major species from the reactant and product as a colorless oil by repeated extractions of the reaction solution with pentane. This oil was identified as *cis,mer*-$RuH_2(CO)(PMe_3)_3$ (**7**) by comparison of the ^1H, ^{13}C, and ^{31}P NMR spectra of the isolated species with those of an authentic sample.[19] *cis,mer*-$RuH_2(CO)(PMe_3)_3$ (**7**) was prepared independently by bubbling of CO through a solution of *mer*-$RuH(\eta^2\text{-}H_2BH_2)(PMe_3)_3$ in pentane.

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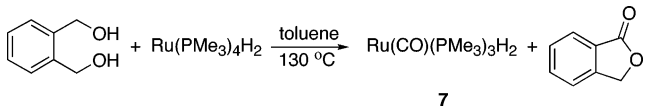
Scheme 5



Scheme 6

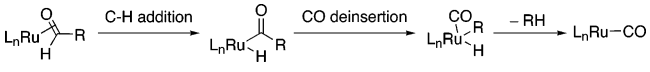
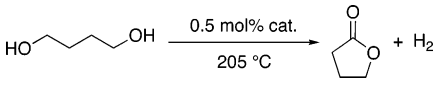


Table 2. Conversion of 1,4-Butanediol to γ-Butyrolactone Catalyzed by Ruthenium Bisphosphine Diamine Complexes and Shvo Complexes[a]



entry	catalyst	time (h)	ratio (diol:GBL)[b]
1	Shvo dimer (**12**)	12	13:87
2	Shvo amide analogue (**13**)	10	77:1
3	*trans*-RuHCl(tmen)(BINAP) (**14**)	10	7:67
4	(DPPF)$RuCl_2$(eda) (**15**)	10	31:69
5	(DIOP)$RuCl_2$(eda) (**16**)	10	0:97
6	$(PPh_3)_2RuCl_2$(eda) (**17**)	10	19:91
7	$(PMe_3)_2RuCl_2$(eda) (**18**)	10	0:99

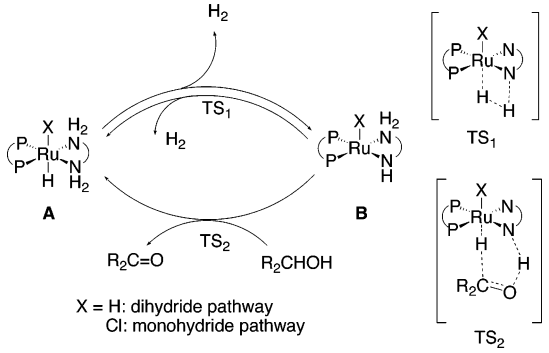
[a] Reaction conditions: catalyst 0.005 mmol and 1.1 mmol of 1,4-butanediol were heated at 205 °C for 10−12 h in a capped vial. [b] Ratios determined by GC. When the sum of the values is less than 100%, other products were observed in the GC trace. eda = ethylenediamine, tmen = tetramethylethylenediamine.

The formation of $RuH_2(CO)(PMe_3)_3$ (**7**) in the catalytic system can be rationalized by the mechanism in Scheme 6. The aldehyde generated by the dehydrogenation process can undergo oxidative addition to ruthenium to give a hydrido acyl Ru complex. Deinsertion of CO would then give an alkyl carbonyl complex, which would undergo reductive elimination of alkane to form a ruthenium carbonyl complex. The generation of CO ligands from alcohols is relatively common,[18] and this pathway for catalyst degradation was noted by Murahashi and co-workers during their studies on the dehydrogenation of primary alcohols to esters catalyzed by $RuH_2(PPh_3)_4$.

We evaluated the reactivity of $RuH_2(CO)(PMe_3)_3$ (**7**) for the dehydrogenation of 1,4-butanediol to γ-butyrolactone to determine if it was an active or inactive form the catalyst. This complex was reactive as a catalyst and was one of the catalysts that exhibited the highest turnover numbers (Table 2). These observations suggest that conversion of the complexes with only phosphines as dative ligands to complexes with a combination of phosphines and carbonyls as dative ligands is facile. Although we could not confidently assign a signal to a bisphosphine dicarbonyl ruthenium complex, we suspected that the bisphosphine dicarbonyl complex would be less reactive than the monocarbonyl compound and would serve as a pathway for catalyst deactivation. Dissociation of ligand would be slow from this species that contains two strong electron donors and two strong π-acceptors. Thus, we sought ruthenium catalysts that would not be converted to carbonyl compounds.

An Approach without Alkoxide Decomposition: Dehydrogenation by the Outer-Sphere Bifunctional Mechanism. To avoid the generation of

Scheme 7



carbonyl ligands by β-hydrogen elimination of alkoxides and activation of the resulting aldehydes, we sought catalysts for the dehydrogenative cyclization that would react by a pathway without alkoxide ligands and that would be less likely to add aldehyde C−H bonds. Complexes that react through the metal−ligand bifunctional mechanism could catalyze the dehydrogenation without an acceptor and without generation of carbonyl ligands (Scheme 7).

The proposed cycle for dehydrogenation involves two intermediates and runs in the opposite direction of the catalytic cycle for the hydrogenation of ketones. The NH proton and the Ru hydride in complex A combine to form molecular hydrogen and complex B. The amide nitrogen and the metal center in complex B then combine with the alcohol to form a six-membered transition state TS_2 that generates ketone and the starting diamine complex.

Catalytic Studies with Complexes that Operate with an Outer-Sphere Mechanism. Results on the conversion of 1,4-butanediol to γ-butyrolactone catalyzed by complexes that are capable of reactivity through an outer-sphere mechanism are summarized in Table 2. Preliminary experiments with CATHy complexes[20] (**8**−**11**) as catalysts for the acceptorless dehydrogenation of 1,4-butanediol to γ-butyrolactone generated little or no γ-butyrolactone. The Shvo dimer[21] (**12**), the amino analogue of the Shvo amide[22] (**13**), and *trans*-RuHCl(tmen)(BINAP)[23] (**14**; tmen = tetramethylethylenediamine, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) with a diamine that lacks β-hydrogens were also evaluated as catalysts for the conversion of 1,4-butanediol to γ-butyrolactone. Each reacted with low to moderate yields and slow rates (Table 1). We suspected that the low activity of the amino analogue of Shvo's compound **13** and certain CATHy complexes for the dehydrogenative cyclization results from their low stability at the high temperatures required to drive the reaction to completion.

We reasoned that the bisphosphine diamine complexes related to those for asymmetric hydrogenation developed by Ikariya and Noyori, but containing alkylphosphine ligands, might be able to catalyze the dehydrogenation more efficiently. As noted above, complexes with alkylphosphines usually exhibit better stability at high temperature than complexes of arylphosphines. In addition, complexes with a combination of phosphine and diamine ligands have been shown to catalyze hydrogenation through an outer-sphere mechanism. Thus, we set out to synthesize a series of simple bisalkylphosphine diamine complexes (**15**−**18**).

Scheme 8

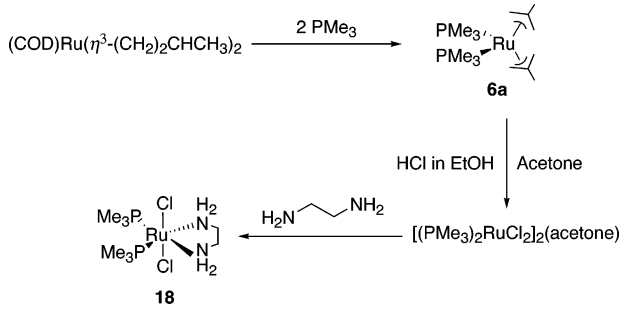


Table 3. Three Catalysts that Exhibit High Turnover Numbers

entry	catalyst	time (h)	TON
1	$RuH_2(PMe_3)_4$ (**1**)	40	3780[a]
2	$RuH_2(CO)(PMe_3)_3$ (**7**)	40	3170[a]
3	*cis*-$(PMe_3)_2RuCl_2$(eda) (**18**)	40	4360[a]
4	*cis*-$(PMe_3)_2RuCl_2$(eda) (**18**)	48	17 000[b]

[a] Reaction conditions: 0.014 mmol of catalyst and 61 mmol of 1,4-butanediol were heated at 205 °C under N_2 for 40 h in an open system. [b] Reaction conditions: 0.014 mmol of catalyst and 240 mmol of 1,4-butanediol were heated at 205 °C under N_2 for 48 h in an open system.

Noyori et al. reported three routes to prepare the bisphosphine diamine ruthenium hydrogenation catalysts.[11] Complexes **15** and **16** were synthesized in a manner similar to the synthesis of (binap)$RuCl_2$(DPEN) (DPEN = 1,2-diphenylethylenediamine) reported by Noyori, which involved treatment of [$RuCl_2$(diphosphine)-$(dmf)_n$] with 1.1 equiv of a diamine. Triphenylphosphine complex **17**, which was prepared to test the activity versus complexes of alkylphosphines, was synthesized according to a literature procedure from $RuCl_2(PPh_3)_3$. To prepare $(PMe_3)_2RuCl_2$(eda) (**18**, eda = ethylenediamine), (COD)Ru(η^3-2-methallyl)$_2$ (COD = 1,5-cyclooctadiene) was treated with 2 equiv of PMe_3 to generate $(PMe_3)_2$Ru(η^3-2-methallyl)$_2$ (**6a**) in 77% isolated yield. This complex was converted to *cis*-$(PMe_3)_2RuCl_2$(eda) (**18**) in 54% yield by the reaction of $(PMe_3)_2$Ru(η^3-2-methallyl)$_2$ (**6a**) with 2 equiv of ethanolic HCl in acetone, followed by reaction of the resulting material with 1 equiv of ethylenediamine (eda) in DMF at room temperature for 1 h (Scheme 8).

Complexes **15**, **16**, and **17** exhibited good to excellent activities without added base (Table 1). Although the addition of base activates these compounds for hydrogenation at low temperatures,[9,24] addition of a base inhibited the dehydrogenation reaction at high temperatures.

The complex *cis*-$(PMe_3)_2RuCl_2$(eda) (**18**) was more active than any catalyst reported previously for the conversion of 1,4-butanediol to γ-butyrolactone. The reaction of 5.5 g of 1,4-butanediol catalyzed by 0.014 mmol of catalyst **1**, **7**, and **18** at reflux (205 °C) for 40 h generated γ-butyrolactone in 87% (TON: 3780), 73%

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(24) Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002**, *124*, 6508−6509.

(TON: 3170), and 100% (TON: 4360) yield, respectively. Furthermore, the reaction of 22 g of 1,4-butanediol catalyzed by 5.4 mg (0.0058 mol %) of *cis*-$(PMe_3)_2RuCl_2$(eda) (**18**) at reflux (205 °C) for 48 h generated γ-butyrolactone in 100% yield. This yield corresponds to a turnover number of 17 000. This turnover number constitutes a commercially viable method to generate γ-butyrolactone from the commodity material 1,4-butanediol.

Conclusion

Through catalyst design and identification of potential pathways for catalyst degradation, we have identified several Ru complexes that are highly reactive and thermally stable as catalysts for the dehydrogenative cyclization of 1,4-butanediol to γ-butyrolactone without hydrogen acceptor or solvent. An alkylphosphine analogue of Noyori's catalysts for alcohol dehydrogenation catalyzed the acceptorless dehydrogenation of 1,4-butanediol to γ-butyrolactone with high selectivity and high turnover numbers. This route to γ-butyrolactone eliminates the need for stoichiometric amount of oxidant, lacks solvent, and uses a reagent—1,4-butanediol—formed from butadiene, acetic acid, and hydrogen.[1]

Experimental Section

General Procedures. Unless otherwise noted, all reactions, recrystallizations, and routine manipulations were performed at ambient temperature in an argon-filled glovebox or by using standard Schlenk techniques. Pentane, benzene, toluene, tetrahydrofuran, and diethyl ether were dried by passage through solvent purification columns (Innovative Technology, MA).[25] Deuterated solvents for use in NMR experiments were obtained from Cambridge Isotope Laboratories (CIL) and were stored under static vacuum over purple sodium benzophenone ketyl and were vacuum transferred before use. Acetone was dried over $CaSO_4$ and was vacuum transferred. Chloroform was dried over P_2O_5 and was vacuum transferred. CD_2Cl_2 was dried over CaH_2 and was vacuum transferred.

^1H NMR spectra were obtained at 400 or 500 MHz. $^{13}C\{^1H\}$ NMR spectra were obtained at 100.6 or 125.8 MHz. $^{31}P\{^1H\}$ NMR spectra were obtained at 162, 122, or 202 MHz. ^1H, ^{13}C, and ^2H NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and were referenced to residual protiated (^1H) or deuterated solvent (^{13}C) or natural abundance deuterated solvent (^2H). ^{31}P NMR chemical shifts were referenced to an external sample of 85% H_3PO_4. GC analyses were performed using a DB-1301 narrow bore column. Response factors were calculated from the ratios of pure product to added naphthalene in ^1H NMR spectra and GC traces.

Materials. The reagents $RuH_2(PMe_3)_4$,[26] (bisphosphine)Ru(2-methylallyl)$_2$ complexes,[27] *trans*-RuHCl(tmen)(BINAP) (tmen = tetramethylethylenediamine),[23] $RuH_2(PPh_3)_4$,[28] $RuH_2(PEt_3)_4$,[29] $RuH_2(PBu_3)_4$,[30] $RuH_2(DMPE)_2$ (DMPE = 1,2-bis(dimethylethylphosphino)ethane),[31] CATHy catalysts,[20] Shvo dimer,[21] Shvo amide analogue,[22] $RuCl_2(CO)(PMe_3)_3$, and $RuCl_2(CO)_2(PMe_3)_2$[32] were prepared by literature procedures.

1,2-Bis(dimethylphosphino)ethane (Strem), ethylenediamine (Aldrich), 1,4-butanediol (Aldrich), and (COD)Ru(η^3-$(CH_2)_2$-$CHCH_3)_2$ (COD = 1,5-cyclooctadiene) (Acros) were used as received without further purification. Hydrogen (zero grade) was obtained from Airgas. 1,3-Propanediol and 1,4-butanediol were purchased from Aldrich and degassed prior to use. All other chemicals were used as received from commercial suppliers.

Representative Procedure for the Dehydrogention of 1,4-Butanediol at 205 °C on a Small Scale. In a drybox, the ruthenium catalyst (0.0057 mmol) was suspended in 0.10 mL (1.1 mmol) of 1,4-butanediol in a screw-capped vial. The reaction mixture was stirred at 205 °C for 12 h. The vial was allowed to cool to room temperature. A small amount (15.0 mg) of the reaction mixture and naphthalene (1.8 mg, 0.0491 mmol) were weighed and dissolved in dichloromethane, and an aliquot was removed and analyzed by GC.

General Procedure for the Dehydrogention of 1,4-Butanediol at 205 °C on a 60 mmol Scale. In a drybox, the ruthenium catalyst (0.014 mmol) was suspended in 5.5 g or in 22 mL of 1,4-butanediol (61 or 240 mmol) in a 25 or 100 mL round-bottom flask. The reaction mixture was stirred at 205 °C for 48 h under nitrogen. The resulting product was analyzed by GC.

Synthesis of $(PMe_3)_2Ru(\eta^3$-$(CH_2)_2CHCH_3)_2$ (6a). To a pentane suspension of (COD)Ru(η^3-$(CH_2)_2CHCH_3)_2$ (150 mg, 0.470 mmol) was added 1 mL of a 1.0 M solution of PMe_3 in toluene (1.0 mmol). The suspension was heated at 80 °C for 5 h. Evaporation of the solvent in vacuo yielded the title complex (132 mg, 0.363 mmol, 77%) as a yellow solid. ^1H NMR (400 MHz, C_6D_6): δ 0.69 (d, J = 13.6 Hz, 2H), 0.98 (d, J = 13.6 Hz, 18H), 1.23 (d, J = 15.2 Hz, 2H), 1.35 (br, 2H), 2.10 (d of t, J = 3.2 Hz, 2H), 2.15 (s, 6H). $^{31}P\{^1H\}$ NMR (202.4 MHz, C_6D_6): δ 6.47. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 19.79 (t, J = 13.4 Hz), 20.04 (t, J = 14.1 Hz), 27.13 (s), 37.79 (t, J = 5.0 Hz), 44.25 (quin, J = 10.2 Hz), 92.47(s). Anal. Calcd for $C_{14}H_{32}P_2Ru$: C, 46.27; H, 8.88. Found: C, 46.13; H, 8.80.

Synthesis of (DMPE)Ru(η^3-$(CH_2)_2CHCH_3)_2$ (6b). (COD)Ru(η^3-$(CH_2)_2CHCH_3)_2$ (150 mg, 0.47 mmol) and 1,2-bis(dimethylphosphino)ethane (80 mg, 0.53 mmol) were dissolved in pentane (2 mL), and the suspension was heated at 80 °C for 5 h. The solution was filtered, and the solvent was evaporated in vacuo. The resulting solid was recrystallized in pentane at −35 °C to give a colorless solid (50 mg, 0.138 mmol, 29%). ^1H NMR (400 MHz, C_6D_6): δ 0.57 (d, J = 7.2 Hz, 6H), 0.78 (d, J = 15.6 Hz, 2H), 1.04 (d, J = 7.2 Hz, 2H), 1.151−1.255 (m, 4H), 1.28 (d, J = 8.4 Hz, 6H), 1.46 (s, 2H), 2.12 (q, J = 2.8 Hz, 2H), 2.20 (s, 6H). $^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6): δ 48.75. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 10.17 (m), 22.60 (d of t, J_1 = 25.6 Hz, J_2 = 9.0 Hz), 27.08 (s), 31.29 (d of d, J_1 = 23.7 Hz, J_2 = 22.3 Hz), 34.22 (t, J = 4.1 Hz), 39.92 (d of t, J_1 = 20.1 Hz, J_2 = 13.2 Hz), 94.20 (s). Anal. Calcd for $C_{14}H_{30}P_2Ru$: C, 46.53; H, 8.37. Found: C, 46.42; H, 8.29.

Synthesis of $RuCl_2(PMe_3)_2$(eda) (18). Into a 20 mL vial was placed $(PMe_3)_2Ru(\eta^3$-$(CH_2)_2CHCH_3)_2$ (200 mg, 0.55 mmol). Acetone (5 mL) and HCl in ethanol (1 M, 1.3 mL) were added, and the mixture was stirred at room temperature for 2 h. The resulting orange solution was evaporated under vacuum. Degassed DMF (6 mL) and ethylenediamine (100 μL, 1.50 mmol, 2.7 equiv) were added to the residue, and the resulting solution was stirred at room temperature for 3 h. The solvent was removed in vacuo, and the solid was crystallized by layering the concentrated toluene solution with pentane at −35

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°C (115 mg, 0.300 mmol, 54%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.27 (t, J = 4.0 Hz, 18H), 2.25 (s, 4H, $2CH_2$), 2.57 (s, 4H, $2NH_2$). ^{31}P{^{1}H} NMR (202.4 MHz, C_6D_6): δ 21.01 (s). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 17.68 (t, J = 13.5 Hz), 42.97 (s). Anal. Calcd for $C_8H_{26}P_2Cl_2N_2Ru$: C, 25.01; H, 6.82; N, 7.29. Found: C, 24.96; H, 6.77; N, 7.20.

Synthesis of (DPPF)RuCl$_2$(eda) (14). Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed $[RuCl_2(C_6H_6)]_2$ (129 mg, 0.258 mmol) and DPPF (305 mg, 0.55 mmol). This material was suspended in 10 mL of degassed DMF and stirred under argon at 100 °C for 10 min to form a reddish brown solution. After the solution was cooled to room temperature, ethylenediamine (40 μL, 0.60 mmol) was added, and the mixture was stirred for 1 h. The solvent was evaporated in vacuo. The residue was dissolved in 5 mL of CH_2Cl_2, and the turbid solution was filtered through Celite. The filtrate was concentrated to about 1 mL, and upon addition of ether a yellow powder was obtained. The supernatant was removed by pipet, and the resulting yellow solid was dried under reduced pressure to give **14** (274 mg, 0.35 mmol, 68% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.66 (s, 4H), 2.71 (s, 4H), 4.20 (s, 4H), 4.63 (s, 4H), 7.27−7.37 (m, 12H), 7.78−7.82 (m, 8H). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 49.06 (s). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 43.53 (s) 70.33 (t, J = 2.5 Hz), 76.49 (t, J = 3.4 Hz), 87.59 (t, J = 24.7 Hz), 127.55 (t, J = 4.2 Hz), 129.25 (s) 134.64 (t, J = 5.1 Hz), 139.29 (t, J = 18.5 Hz). Anal. Calcd for $C_{36}H_{36}Cl_2FeN_2P_2Ru$: C, 54.98; H, 4.61; N, 3.56. Found: C, 54.83; H, 4.74; N, 3.70.

Synthesis of (DIOP)RuCl$_2$(eda) (15). Into a 20 mL scintillation vial equipped with a magnetic stir bar were placed $[RuCl_2(C_6H_6)]_2$ (129 mg, 0.258 mmol) and DIOP (273 mg, 0.55 mmol). This material was suspended in 10 mL of degassed DMF, and the resulting solution was stirred under argon at 100 °C for 10 min. The solution turned reddish brown. After the solution was cooled to room temperature, ethylenediamine (40 μL, 0.60 mmol) was added, and the mixture was stirred for 1 h. The solvent was evaporated in vacuo. The residue was dissolved in 5 mL of CH_2Cl_2, and the resulting turbid solution was filtered through Celite. The filtrate was concentrated to about 1 mL. Upon addition of ether, a yellow powder was obtained. The supernatant was removed by pipet, and the resulting yellow solid was dried under reduced pressure to give **15** (297 mg, 0.41 mmol, 79% yield). Too many aliphatic protons: ^{1}H NMR (400 MHz, C_6D_6): δ 1.40 (s, 6H), 2.00 (d, J = 4.0 Hz, 4H), 2.45 (br, 2H), 2.60 (br, 2H), 3.30−3.38 (m, 4H), 4.66 (s, 2H), 7.00 (m, 12H), 7.72−7.75 (m, 4H), 7.82−7.87 (m, 4H). ^{31}P{^{1}H} NMR (202.4 MHz, C_6D_6): δ 37.92 (s). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 27.35 (s), 32.92 (t, J = 14.7 Hz), 43.07 (s) 78.02 (t, J = 6.3 Hz), 107.61 (s), 128.10 (t, J = 4.3 Hz), 128.14 (t, J = 4.3 Hz), 128.95 (s) 129.35 (s) 132.57 (t, J = 4.3 Hz), 133.91 (t, J = 5.0 Hz), 138.20 (t, J = 18.2 Hz), 139.59 (t, J = 19.3 Hz). Anal. Calcd for $C_{33}H_{40}Cl_2N_2O_2P_2Ru$: C, 54.25; H, 5.52; N, 3.83. Found: C, 54.11; H, 5.34; N, 3.93.

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