Mechanistic Aspects of Formation of Chiral Ruthenium Hydride Complexes from 16-Electron Ruthenium Amide Complexes and Formic Acid: Facile Reversible Decarboxylation and Carboxylation

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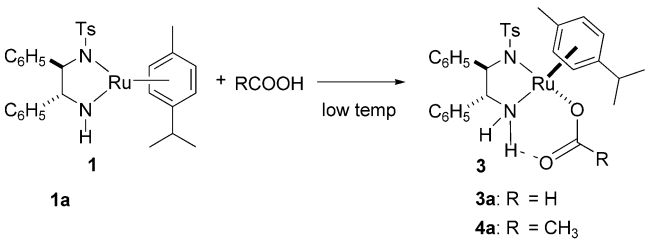
Abstract: The 16-electron amide complex, Ru[(*R,R*)-TsNCHPhCHPhNH](η⁶-*p*-cymene) (Ts = *p*-toluenesulfonyl, Ph = C_6H_5) readily reacts with formic acid to give the corresponding formate complex, which subsequently undergoes decarboxylation leading to the hydride complex with release of CO_2. The reaction of this hydride complex with CO_2 under mild reaction conditions, a pressure of 10 atm and even at −78 °C, proceeds rapidly to give the corresponding formate complex almost quantitatively. Thus, the reversible decarboxylation and carboxylation takes place with or without the aid of a metal-NH bifunctional effect of the Ru complexes.

Keywords: carbon dioxide insertion; decarboxylation; M-NH bifunctional effect; ruthenium formate; ruthenium hydride

A well-defined chiral amido ruthenium complex, Ru[(*R,R*)-TsNCHPhCHPhNH](η⁶-*p*-cymene)[1] (**1a**, Ts = *p*-toluenesulfonyl, Ph = C_6H_5), has sufficient Brønsted basicity to effectively deprotonate hydrogen donors such as 2-propanol or HCOOH giving a chiral hydrido-amine complex, RuH[(*R,R*)-TsNCHPhCHPhNH$_2$](η⁶-*p*-cymene) (**2a**), in a highly stereoselective manner.[1] This chiral hydrido ruthenium complex **2a** readily reacts with ketonic substrates to provide optically active alcohols with regeneration of the amide complex **1a**. Thus, enantioselective hydrogen transfer between the hydrogen donors and ketones takes place catalytically with these two isolable complexes as catalytic intermediates. In particular, in the reaction with 2-propanol as a hydrogen source, experimental results[1d,2] as well as computational analysis[3] revealed that hydrogen transfer proceeds reversibly *via* a pericyclic six-membered transition state. In contrast to the reaction in 2-propanol,[1–3] the detailed mechanism of the hydrogen transfer from HCOOH to carbonyl compounds has not been clarified, even though asymmetric ketone reduction with HCOOH is a practical procedure for the synthesis of optically active alcohols.[4] We now report on mechanistic aspects of the reaction of the amide complex **1a** with HCOOH leading to the formato-amine complex, Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH$_2$)](η⁶-*p*-cymene) (**3a**),[3c,5] which is readily decarboxylated to give the hydrido-amine complex **2a** and CO_2, and the reverse reaction of the hydride complex **2a** with CO_2.[6] This is the first experimental demonstration of the NH-assisted formal CO_2 insertion into the Ru–H bond.

The 16-electron amide complex **1a** has been proven to react smoothly with one equivalent of HCOOH at a low temperature (below −30 °C) to give the formate complex **3a** as a single diastereomer as shown in Scheme 1. The ^{1}H NMR spectrum of **3a** displays two non-equivalent NH protons and a OCHO proton at δ = 6.28, 8.96 ppm, and 8.19 ppm (THF-d_8, −40 °C), respectively.

Unfortunately, single-crystal X-ray crystallographic analysis of **3a** failed because of thermal instability of **3a**. However, some structural information could be obtained from an analogous acetate complex **4a**, which was prepared from a reaction of the amide complex **1a** and



Scheme 1.

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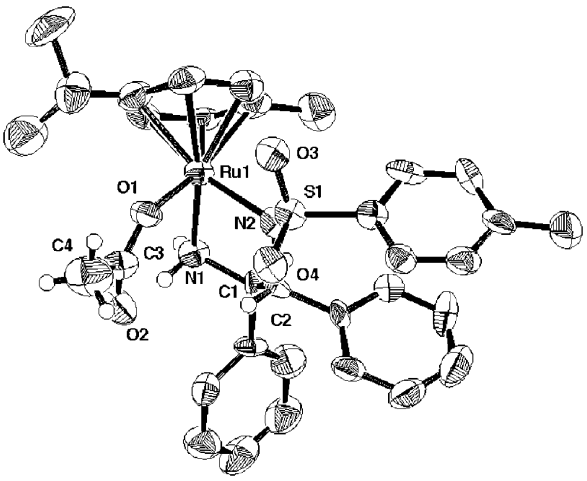
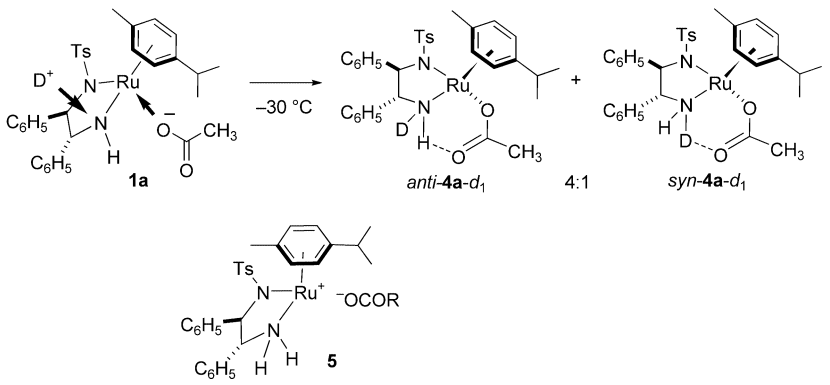


Figure 1. ORTEP view of $Ru(OCOCH_3)[(R,R)\text{-}TsNCHPhCHPhNH_2](\eta^6\text{-}p\text{-cymene})$ (**4a**). Selected bond lengths (Å): Ru(1)–O(1), 2.114(7); Ru(1)–N(1), 2.092(8); Ru(1)–N(2), 2.150(8); O(1)–C(3), 1.27(1); O(2)–C(3), 1.23(1). Selected bond angles (deg): N(1)–Ru(1)–N(2), 78.6(3); N(1)–Ru(1)–O(1), 88.9(3); N(2)–Ru(1)–O(1), 86.7(3); Ru(1)–N(1)–C(1), 111.6(6); Ru(1)–N(2)–C(2), 112.5(6). Priority for the assignment of absolute configuration at Ru: *p*-cymene > $OCOCH_3$ > NTs > NH_2.

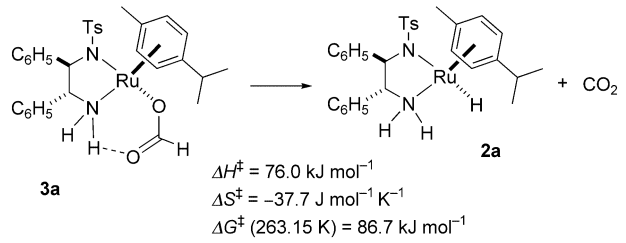
acetic acid in a manner similar to the synthesis of **3a**. The X-ray crystallographic analysis of complex **4a**,[7] as illustrated in Figure 1, confirmed that it has a three-legged piano stool coordination environment with *p*-cymene, amino, sulfonamido, and acetato ligands. The chirality of the (*R,R*)-diamine ligand determines the *S* configuration around the central metal, as observed in the hydride complex **2a**.[1d] Notably, there is a short $H_2N\cdots O{=}C$ distance of 2.77 Å, which is ascribed to an intramolecular hydrogen bond.[8] Morris recently reported that a reaction of Ru amide complex, $RuH(PPh_3)_2(NH_2CMe_2CMe_2NH)$ (Me = CH_3), with formic acid gave a similar hydrogen-bonded formate complex, *trans*-$RuH(OCHO)(PPh_3)_2(NH_2CMe_2CMe_2NH_2)$, which was determined by single-crystal X-ray analysis as well as NMR and IR spectroscopy.[3c] The ^{1}H NMR spectrum of **4a** shows two non-equivalent NH protons at $\delta = 4.48$ and 9.59 ppm (CD_2Cl_2, r.t.) like the formate complex **3a**. The NH signal at the lower field can be assigned to the proton that interacts with an oxygen atom of the acetato ligand in **4a** possibly through hydrogen bonding as observed in related complexes.[1d,9b, c,10] The IR spectrum of **4a** shows a characteristic C=O stretching frequency at 1567 cm^{-1}, indicating that **4a** has a hydrogen-bonded acetato group.

Low temperature NMR studies have suggested that the addition of the O–H bond of HCOOH or CH_3COOH to the Ru–N bond of the amide complex **1a** proceeds in a stepwise manner *via* an ion pair intermediate (**5**) (Scheme 2)[9a] leading to the kinetically favorable carboxylate complex **3a** or **4a**, as observed in the reaction of the complex **1a** or the analogous amido Ir complex with acidic compounds.[9b, c] For example, the ^{1}H NMR spectrum of the reaction of **1a** with one equivalent of CH_3COOD at $-30\,^\circ C$ in CD_2Cl_2 showed two signals due to NH_2 protons in the deuterated complex **4a**-d_1 at $\delta = 4.83$ and 8.92 ppm with a 1:4 ratio of relative intensity, indicating that the *anti*-**4a**-d_1 was preferentially formed at the lower temperature, as shown in Scheme 2.

An increase in the temperature of the formate complex **3a** in THF-d_8 resulted in formation of **2a**[1d] indicating that the hydride complex **2a** is formed through the decarboxylation of the intermediate **3a** even under the conditions of catalytic asymmetric transfer hydrogenation (Scheme 3). Monitoring of the ^{1}H NMR spectrum of the decarboxylation of **3a** in THF-d_8 at the temperature range from 258.15 K to 273.15 K revealed that the rate of this transformation was the first-order dependence on **3a**.[11] The activation parameters for decarboxylation of **3a**,[12] $\Delta H^{\ddagger} = 76.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -37.7$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}$ (263.15 K) = 86.7 kJ mol^{-1}, which are comparable to the values reported in the literature,[13] were determined from linear first-order plots obtained at several different temperatures. Based on the kinetic data involved with the negative entropy value, there are three possible pathways for the decarboxylation: formato anion dissociation leading to an ion pair (**5**),[9] η^6-arene ring slippage to η^4-arene, or NH_2



Scheme 2.

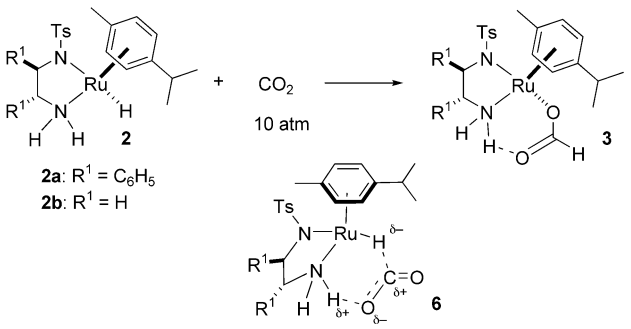


Scheme 3.

ligand dissociation providing a vacant site, followed by β hydrogen elimination, respectively.

Although the precise mechanism of the decarboxylation has not yet been clarified, further valuable information on the relevant reverse reaction, the formal insertion of CO_2 into the Ru–H bond in the hydride complex **2a** and the analogous hydride complex, RuH($TsNCH_2CH_2NH_2$)(η^6-*p*-cymene) (**2b**), can be obtained. The reaction of **2a** or **2b** with CO_2 under mild reaction conditions, a pressure of 10 atm and even at $-78\,^{\circ}C$, proceeded rapidly to give the corresponding formate complex **3a** or **3b**, respectively, as shown in Scheme 4. It should be noted that the presence of the NH moiety in the ligands is crucially important for the reaction with CO_2 as observed in the effective transfer hydrogenation of carbonyl compounds to alcohols.[1] The NH group in the amine ligand possibly participates in the CO_2 activation through the formation of a hydrogen bonding network (**6** in Scheme 4), as reported previously in a rapid hydrogenation of CO_2 catalyzed by Ru–$P(CH_3)_3$ complexes.[14–15] Jessop recently reported an alcohol-assisted CO_2 hydrogenation,[16] where a highly acidic alcohol participates in activation of CO_2. The carboxylation of the analogous hydride complex bearing the $N(CH_3)_2$ group in the amine ligand, RuH[$TsNCH_2CH_2N(CH_3)_2$](η^6-*p*-cymene) provided no corresponding formate complex. Thus, the hydrido ligand directly migrates to the carbon center of CO_2 possibly *via* the pericyclic six-membered transition state leading to a formato anion possibly through an ion pair, as predicted by computational analysis of a similar Ru complex system.[14c] A reacting CO_2 is not necessarily bound directly to the Ru center.[1d,2,3,14]

In summary, the 16-electron amide complex **1a** readily reacts with HCOOH to give the corresponding formate



Scheme 4.

complex **3a**, which subsequently undergoes decarboxylation leading to the hydride complex **2a** with release of CO_2. Decarboxylation of the formate complex and CO_2 insertion into the Ru–H bond giving the formate complex proceed reversibly possibly through the same intermediate or transition state with or without the aid of the metal-NH bifunctional effect. Since this formal CO_2 insertion reaction proceeds, the CO_2 generated in the asymmetric reduction with formic acid should be effectively removed from the catalyst system.

Experimental Section

All manipulations were conducted under argon atmosphere. Deuterated NMR solvents were dehydrated and degassed by appropriate methods. Amide complexes and hydride complexes were prepared according to the procedure reported in the literature.[1d]

Formation of 3a

A THF-d_8 solution (5.36×10^{-2} M) of formic acid (2.20×10^{-2} mL, 1.77×10^{-5} mol) was added to a solution of Ru[(*R,R*)-TsNCHPhCHPhNH](η^6-*p*-cymene) (**1a**) (1.07×10^{-2} g, 1.78×10^{-5} mol) containing 1,3,5-trimethoxybenzene or dihexyl ether as an internal standard in an NMR tube at $-78\,^{\circ}C$. The solution color turned from purple to yellow. The reaction product was determined to be Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**3a**) by a comparison with NMR data of the analogous acetate complex **4a** (described below). Although the complex was a crystalline material at low temperature, X-ray crystal structural analysis and elemental analysis have not yet been successfully performed because of the thermal instability and moisture sensitivity.

Spectral data for Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**3a**): ^{1}H NMR (300.4 MHz, THF-d_8, $-40\,^{\circ}C$): $\delta = 1.33$ [d, $^3J_{HH} = 6.60$ Hz, 6H, $(CH_3)_2CH$ in *p*-cymene], 2.22 (s, 3H, CH_3 in *p*-cymene), 2.27 (s, 3H, CH_3 in Ts), 2.87 [m, 1H, $CH(CH_3)_2$ in *p*-cymene], 3.42 (m, 1H, $HCNH_2$), 3.72 (d, $^3J_{HH} = 11.2$ Hz, 1H, *H*CN-Ts), 5.40, 5.59, 5.77, 6.00 (each d, $^3J_{HH} = 5.37$ Hz, $^3J_{HH} = 6.09$ Hz, $^3J_{HH} = 5.37$ Hz, $^3J_{HH} = 6.09$ Hz, CH_{arom} in *p*-cymene), 6.28(br. d, $^3J_{HH} = 7.32$ Hz, 1H, HCNH*H*), 6.66–7.20 [14H, *p*-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$], 8.19 (s, 1H, OC*H*O), 8.96(br. dd, 1H, N*H*H); $^{13}C\{^1H\}$ NMR (75.6 MHz, THF-d_8, $-30\,^{\circ}C$): $\delta = 18.7$, 21.3, 23.8, 27.1, 30.9 [$CH_3C_6H_4CH(CH_3)_2$, CH_3 in Ts], 70.7, 74.4 [$TsNCH(C_6H_5)CH(C_6H_5)NH_2$], 79.5, 81.0, 84.6, 88.3, 92.8, 104.0 ($CH_3C_6H_4CH(CH_3)_2$), 126.5–144.7 [*p*-$CH_3C_6H_4SO_2NCH(C_6H_5)CH$ $(C_6H_5)NH_2$], 173.5(O*C*HO).

Synthesis of Ru(OCOCH$_3$)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (4a)

Acetic acid (1.50×10^{-2} mL, 2.62×10^{-4} mol) was added to a solution of Ru[(*R,R*)-TsNCHPhCHPhNH](η^6-*p*-cymene) (**1a**) (1.26×10^{-1} g, 2.10×10^{-4} mol) and CH_2Cl_2 (5 mL) in a 20-mL Schlenk reactor. The solution color changed from purple to yellow. The reaction mixture was vigorously stirred at room

temperature for 2 h. Then, the solvent was removed under reduced pressure. The residue was recrystallized from a mixed solvent of toluene and hexane to give orange crystals, Ru(OCOCH$_3$)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**4a**) (4.94×10^{-2} g, 36% yield). Spectral data for Ru(OCOMe)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**4a**): ^{1}H NMR (300.4 MHz, CD_2Cl_2, r.t.): δ = 1.36 [d, $^3J_{HH}$ = 6.93 Hz, 6H, (C*H*$_3$)$_2$CH in *p*-cymene], 1.93 (s, 3H, C*H*$_3$ in *p*-cymene), 2.23, 2.25 (s, 6H, C*H*$_3$ in Ts, C*H*$_3$COO), 2.88 [m, 1H, C*H*(CH$_3$)$_2$ in *p*-cymene], 3.45 (m, 1H, *H*CNH$_2$), 3.73 (d, $^3J_{HH}$ = 11.1 Hz, 1H, *H*CN-Ts), 4.48 (br. d, $^3J_{HH}$ = 7.20 Hz, 1H, HCNH*H*), 5.28, 5.49, 5.65, 5.82 (each d, $^3J_{HH}$ = 5.73 Hz, $^3J_{HH}$ = 5.85 Hz, $^3J_{HH}$ = 5.61 Hz, $^3J_{HH}$ = 5.85 Hz, C*H*$_{arom}$ in *p*-cymene), 6.66 – 7.24 [14H, *p*-CH$_3$C$_6$*H*$_4$SO$_2$-NCH(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$], 9.59 (br. dd, 1H, N*H*H); ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, r.t.): δ = 18.6, 21.2, 21.8, 23.0, 26.1, 30.9 [*C*H$_3$C$_6$H$_4$*C*H(*C*H$_3$)$_2$, *C*H$_3$ in Ts, *C*H$_3$COO], 69.5, 73.6 [TsN*C*H(C$_6$H$_5$)*C*H(C$_6$H$_5$)NH$_2$], 79.6, 81.8, 83.3, 86.4, 93.5, 103.9 [CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$], 126.5 – 143.2 [*p*-CH$_3$*C*$_6$H$_4$SO$_2$NCH(*C*$_6$H$_5$)CH(*C*$_6$H$_5$)NH$_2$], 183.4 (O*C*OCH$_3$); IR(KBr): ν = 3190 (ν$_{H-N}$), 3063, 3031 (ν$_{H-Carom}$), 2961 (ν$_{H-Caliph}$), 1567 (ν$_{C=O}$), 1390, 1330, 1198, 1176, 1154 cm^{-1} (ν$_{SO_2-N}$); elemental anal. calcd. for $C_{33}H_{38}O_4N_2S_1Ru_1$: C 60.07, H 5.80, N 4.25, S 4.86; found: C 60.12, H 5.70, N 4.17, S 4.76.

Experimental Procedure for Decarboxylation of 3a and Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH(CH$_3$)](η^6-*p*-cymene)

A THF-d_8 solution of (2.44×10^{-2} M in THF-d_8, 0.43 mL) formic acid (1.40×10^{-2} mL, 9.51×10^{-6} mol) was added to a solution of Ru[(*R,R*)-TsNCHPhCHPhNH](η^6-*p*-cymene) (**1a**) (5.70×10^{-3} g, 9.50×10^{-6} mol), dihexyl ether(1×10^{-3} mL) in an NMR tube at the dry-ice-methanol temperature. The disappearance of the peaks due to the formate complex, Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**3a**), was monitored by ^{1}H NMR at 263.15 K. The resulting kinetic data are shown in the supporting information (Figure S1). The observed rate constant value was determined to be $k_{obs} = 4.43 \times 10^{-5}$ s^{-1}.

In a similar manner, the reaction of Ru[(*R,R*)-TsNCHPhCHPhN(CH$_3$)](η^6-*p*-cymene) (6.70×10^{-3} g, 1.09×10^{-5} mol) with formic acid(1.60×10^{-2} mL, 1.09×10^{-5} mol) in THF-d_8 (0.52 mL) gave Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH(CH$_3$)](η^6-*p*-cymene) traced by ^{1}H NMR at 263.15 K. The resulting kinetic data are shown in the supporting information (Figure S2). The observed rate constant value determined was $k_{obs} = 9.99 \times 10^{-5}$ s^{-1}.

The rate constants of the decarboxylation of **3a** were obtained at several different temperatures, 273.15 K, 268.15 K, 263.15 K and 258.15 K and the kinetic parameters was determined as shown in the supporting information (Figure S3). An Eyring analysis of the pseudo-first data gives $\Delta H^{\ddagger} = 76.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -37.7$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger} = 86.7$ kJ mol^{-1}.

Reaction of the Hydride Complex, RuH[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (2a) with CO$_2$

CO_2 gas (16 mL) at 10 atm was introduced into a THF-d_8 solution of RuH[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**2a**) (8.00×10^{-3} g, 1.33×10^{-5} mol) containing 1,3,5-trimethoxybenzene as an internal standard in a pressure-resistant NMR tube at liquid nitrogen temperature. The reaction mixture was put in dry-ice-methanol bath at −78 °C for 3 h and then, the reaction was monitored by ^{1}H NMR at −30 °C. The ^{1}H NMR spectrum of the resulting solution showed that the peaks due to the hydride complex **2a** disappeared and peaks attributed to the formate complex, Ru(OCHO)[(*R,R*)-TsNCHPhCHPhNH$_2$](η^6-*p*-cymene) (**3a**) appeared at the same chemical shifts as those observed in the reaction of the amide complex with formic acid. The reaction was found to proceed quantitatively.

Supporting Information Available

Experimental procedure of formation of formate and acetate complexes, physical and NMR data of the complexes **3a**, kinetic data of decarboxyaltion of **3a** and an X-ray-crystallographic data of **4a**, Ru(OCOCH$_3$)(TsNCH$_2$CH$_2$NH$_2$)(η^6-*p*-cymene), and Ru(OCOCH$_3$)[TsNCH$_2$CH$_2$N(CH$_3$)$_2$](η^6-*p*-cymene).

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[7] An X-ray crystallographic analysis of **4a** was performed. Crystal and structure refinement parameters of **4a**: $C_{33}H_{38}N_2O_4RuS$, $M_r = 659.80$, orthorhombic, space group $P2_12_12_1$ (#19), $a = 14.594(7)$ Å, $b = 24.126(7)$ Å, $c = 8.832(5)$ Å, $V = 3109.8(2)$ Å^3, $Z = 4$, $D_c = 1.41$ g/cm^3, $\mu(MoK\alpha) = 6.10$ cm^{-1}, $T = 233$ K, R_1 (wR_2) = 0.052 (0.129) for 4010 observed reflections ($I > 0.00\sigma(I)$). All hydrogen atoms were calculated from ideal geometries. See Supporting Information.

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[10] Analogous acetate complexes bearing the $TsNCH_2CH_2NH_2$ ligand and the $TsNCH_2CH_2N(CH_3)_2$ ligand were synthesized from the reactions of RuCl-($TsNCH_2CH_2NH_2$)(η^6-*p*-cymene) and RuCl[$TsNCH_2$-$CH_2N(CH_3)_2$](η^6-*p*-cymene) with CH_3COOAg, respectively, and were determined by X-ray crystallographic analysis (see Supporting Information). The C=O stretching frequency appears at 1561 cm^{-1} for the acetate complex with $TsNCH_2CH_2NH_2$ while it shows at1620 cm^{-1} for the complex with $TsNCH_2CH_2N(CH_3)_2$, indicating that the former has a similar hydrogen-bonded acetato group. The chloride, formate and acetate complexes with $TsNCHPhCHPhN(CH_3)_2$, RuCl-[$TsNCHPhCHPhN(CH_3)_2$](η^6-*p*-cymene), Ru(OCHO)-[$TsNCHPhCHPhN(CH_3)_2$](η^6-*p*-cymene) and Ru-($OCOCH_3$)[$TsNCHPhCHPhN(CH_3)_2$](η^6-*p*-cymene) could not be obtained possibly due to thermal instability.

[11] The observed rate constants for decarboxylation of **3a** and Ru(OCHO)[$TsNCHPhCHPhNH(CH_3)$](η^6-*p*-cymene) were 4.43×10^{-5} and 9.99×10^{-5} s^{-1}, respectively. The introduction of a methyl substituent on the nitrogen atom in the diamine ligand caused a slight increase in the rate of the reaction possibly due to steric reasons.

[12] See Supporting Information.

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[15] Recently, Jessop reported an alcohol-assisted CO_2 hydrogenation,[13,14] where a highly acidic alcohol participates in activation of CO_2: P. M. Munshi, A. D. Main, J. C. Linehan, C.-C. Tai, P. G. Jessop, *J. Am. Chem. Soc.* **2002**, *124*, 7963 – 7971.

[16] For CO_2 hydrogenation, see:a) P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **1994**, *368*, 231 – 233; b) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259 – 272; c) W. Leitner, *Angew. Chem., Int. Ed. Engl.,* **1995**, *34*, 2207 – 2221; preliminary experimental results showed that the chloride complex, RuCl($TsNCH_2CH_2NH_2$)(η^6-*p*-cymene), which was the precursor of amide complexes[1] exhibits catalytic activity for the hydrogenation of supercritical CO_2 in the presence of *N′,N′*-dimethylammonium *N,N*-dimethylcarbamate as substrate (S/C = 1,000) at 50 °C for 45 h to give DMF in moderate yield, 69% yield.

