Full Paper

Applied
Organometallic
Chemistry

Received: 4 August 2008 Revised: 16 September 2008 Accepted: 27 October 2008

(www.interscience.com) DOI 10.1002/aoc.1473

Conversion of carbon dioxide to cyclic carbonates using diimine Ru(II) complexes as catalysts

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Cationic diimine Ru(II) complexes were synthesized and tested as catalysts for the formation of cyclic organic carbonates from CO_2 and liquid epoxides (propylene oxide, epichlorohydrine, 1,2-epoxybutane and styrene oxide) which served as both reactant and solvent. The reaction rates not only depended on the type of ligand, but also on reaction conditions such as temperature, pressure, base, the epoxide substrates and the use of an additional solvent. Reaction rates in terms of turnover frequencies up to 4050 $\mathrm{mol_{product}\ mol_{cat.}^{-1}\ h^{-1}}$ at 99% selectivity were achieved by optimizing the diimine ligand as well as the reaction temperature and CO_2 pressure. Consistent with CV measurements, the electron donating group on the *p*-position of the aryl ring accelerated the reaction rate.

Keywords: diimine complexes; ruthenium(II); carbon dioxide fixation; epoxide; cyclic carbonates; electrochemistry

Introduction

Recently the chemical fixation of carbon dioxide received a great deal of attention from the viewpoint of carbon resources and environmental problems.[1–4] One of the most common processes is transformation of carbon dioxide to cyclic carbonates. The cyclic carbonates are widely used as organic synthetic intermediates, aprotic polar solvents, precursors for biomedical applications and as raw materials for engineering plastics.[5] Various catalysts have been developed for the synthesis of cyclic organic carbonates from CO_2 and epoxides, among which several homogeneous and heterogeneized salen complexes,[6] alkali metal halides,[7] organic bases,[8] metal oxides,[9] zeolite,[10] ionic liquids[11] and metal complexes[12] can be mentioned. While the advances have been significant, most of these catalysts currently suffer from low catalyst reactivity, the need for co-solvent or the requirement for high pressure and/or high temperature.

Bidentate diimines are most commonly studied ligand classes in coordination chemistry, since their ease of synthesis with different steric and electronic profiles makes them particularly attractive for catalytic studies.[13] Very recently, Cao and co-workers reported one of the few Ru(II) complexes, the (2,2′-bipy)$RuCl_3(CH_3OH)$ (**A**) as a catalyst for the formation of propylene carbonate with 72% yield (3.0 MPa, 75 °C, 2 h, cetyltrimethylammonium chloride).[14] Tricarbonyl rhenium(I) complex with a pendant pyrrolidinium moiety (**B**) gave only 13% yield (1.5 MPa, 80 °C, 1 h, pyrrolidinium bromide) of propylene carbonate with the equamolar catalyst system loadings. The selectivity is an important phenomenon of the catalyst chemistry.[15] Darensbourg and others noted that coupling of epoxides and carbon dioxide produced either corresponding monomeric or polymeric cyclic carbonates.[16]

However, to the best of our knowledge, simple diimines coordinated to Ru(II) centers have not been used as a catalyst system for chemical fixation of carbon dioxide. The most active catalyst (**2c**) is very atractive for industrial application due to its easy preparation and air-, moisture- and partial heat-resistance (up to 120 °C). Herein we report the synthesis of diimine Ru(II) complexes as homogenous catalysts for selective transformation of carbon dioxide to five-membered cyclic carbonates.

Results and Discussion

Synthesis and Characterization of Diimines (1) and Complexes (2)

With the objective of understanding the influence of their steric and electronic effects, we have prepared a variety of diimines and the synthetic route used for the preparation of the diimine (**1**) and of their Ru(II) complexes **2** shown in Scheme 2. The Schiff bases **1** were prepared by condensation of commercially available alkylic diamines with corresponding aromatic aldehydes in alcoholic media at room temperature. The Schiff bases were recrystallized from methanol–CH_2Cl_2 solution in good yields (85–97%). Schiff bases (**1a**,[17a] **1b**,[17a] **1c**,[17b] **1d**[17c]) have been reported in the literature; **1e** and **1f** were prepared using the same procedure. Ionic Ru(II) complexes (**2**) were synthesized at room temperature by reaction of diimines (**1**) with half-equivalent ruthenium dimer. Mesityl-substituted complexes (**2d–f**) are sensitive to air in solution; however, they are perfectly stable in the solid state. Therefore, these complexes could only be obtained using freshly distilled solvents in argon using standard Schlenk techniques. At the end of reaction, the solvent was evaporated in vacuum to dryness. The reaction mixture was dissolved in CH_2Cl_2 and filtered with cannula on celite to remove the sodium salt(s). The desired products were obtained after concentration of CH_2Cl_2 solutions and then precipitated with diethyl ether.

The diimines (**1**) were fully characterized by IR, ^1H and ^{13}C NMR spectroscopy. The IR spectra of Schiff bases showed peaks

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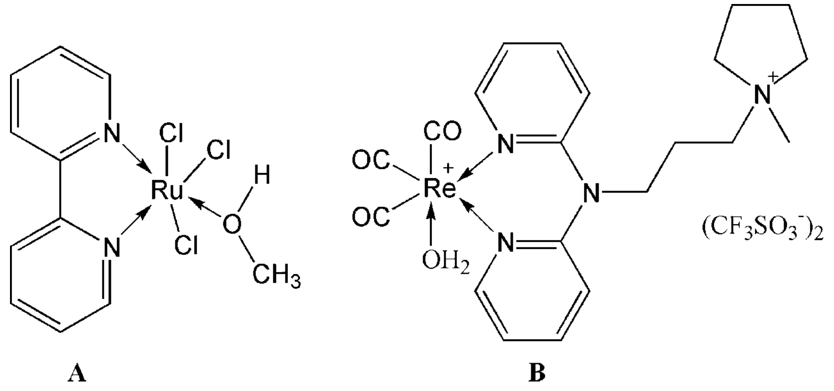
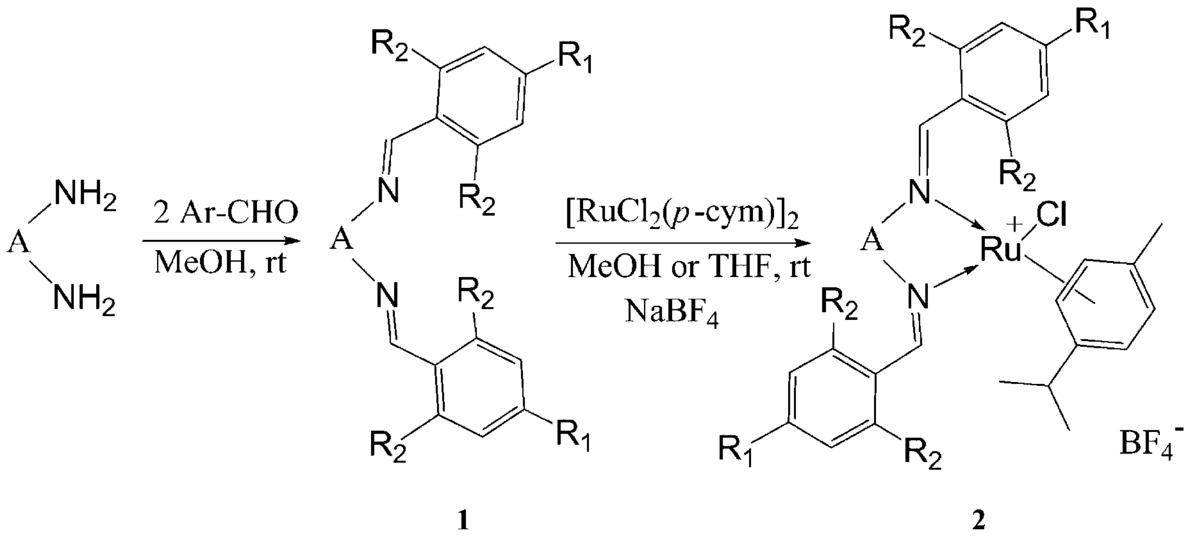


Scheme 1. Diimine-metal complexes as catalysts in literature.



Compound	A	R_1	R_2
a	$-CH_2CH_2-$	NMe_2	H
b	$-CH_2CH_2CH_2-$	NMe_2	H
c	$-CH_2CH_2-$	NEt_2	H
d	$-CH_2CH_2-$	Me	Me
e	$-CH_2CH_2CH_2-$	Me	Me
f	$-CH_2C(CH_2)_2CH_2-$	Me	Me

Scheme 2. Synthetic route to the diimine Ru(II) complexes.

in the υC=N stretching frequency region at 1636–1647 cm^{-1} given in Table 1. The coordination of Schiff bases to Ru(II) through the nitrogen atom was expected to lower the (C=N) frequency (1610–1626).[18,19]

The ^{1}H NMR spectra of the Schiff bases show signals for the proton attached to the imine group and the protons from the aryl rings and proton signals at *ca* 1–2 ppm, indicating the presence of the methyl substituents on the aryl rings of the imine. The characteristic signals of imines (C*H*=N) at 8.64 ppm for **1e** and for**1f** as singlets were also observed. The ^{13}C NMR data for **1** are consistent with the proposed structures. In the ^{13}C NMR (CDCl$_3$) of imines (CH=N) carbon resonances appeared at 161.4 ppm for **1e** and also 161.5 ppm for **1f**. Details of the synthesis and product characterization are given in the Experimental section.

Table 1. Selected IR bands (υ C=N cm^{-1}) of the synthesized compounds **1** and **2** as KBr pellets

	Compounds					
	a	b	c	d	e	f
1	1636	1638	1639	1637	1647	1646
2	1620	1610	1622	1626	1622	1611

Diimine Ru(II) complexes **2** were also characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. In addition, the complex **2d** was characterized by HMQC, COSY and HMBC techniques. In the ^{1}H NMR ($CDCl_3$) spectra of the complexes, characteristic signals of the *p*-cymene group appeared via cyclometallation to ruthenium. The ^{13}C NMR ($CDCl_3$) spectra of these complexes were well defined. In the ^{13}C NMR the imine carbon resonance was found at 174.9, 173.9 and 174.6, 174.7, 179.2 and 179.8, 178.9 and 182.5, 180.6 and 193.2 ppm for complexes **2a, 2b, 2c, 2d, 2e** and **2f**, respectively, and were shifted to higher frequency when compared with the free azomethines. This shift is indicative of coordination, with the transfer of electron density from the imine to the metal center.[18]

Catalytic Studies

The cycloaddition reaction of carbon dioxide with epoxides in the presence of 0.1% **2** was conducted as a model reaction for testing, and the results are compiled in Table 2. It is clear that the structure of the diimine and the nature of the anion influences the yield of the cyclic carbonate (**3**) (entries 1–6). The reaction time, reaction temperature and pressure of CO_2 are also important factors in the yields of cyclic carbonates (Figs 2–4). Figure 1 presents the catalytic activity of different complexes under the same catalytic conditions. Ligand structure has a marked influence on the catalytic activity. The electron donating group on the *p*-position of the imine ligand accelerates the reaction rate.

R = Et, 1,2-epoxybutane (EB); Me, propylene oxide (PO); CH_2Cl, epichloro hydrine (EC); phenyl, styrene oxide (SO). DMAP, 4-dimethylaminopyridine.

The reaction proceeded with efficiencies up to 98.8% yield under considerably milder conditions than other systems based on Ru(II) complex (**A**).[14] The electron-withdrawing groups at the 2-position of the epoxide activated the substrate, while electron-donating substituents deactivated the epoxide.

Table 2. Synthesis of cyclic carbonates from epoxides and CO_2 catalyzed by diimine-Ru(II) complexes **2**

Entries	2	Epoxide R	Solvent	Yield[a]	TON[b]	TOF[c] (h^{-1})
1	**2a**	Et	–	54.0	540	270
2	**2b**	Et	–	69.1	691	346
3	**2c**	Et	–	71.1	711	356
4	**2d**	Et	–	32.0	320	160
5	**2e**	Et	–	30.7	307	154
6	**2f**	Et	–	52.4	524	262
7	**2c**	Et	CH_2Cl_2	21.7	217	109
8	**2c**	Me	–	67.2	672	336
9	**2c**	Ph	–	73.1	730	365
10	**2c**	CH_2Cl	–	98.8	988	494
11	**2c**	CH_2Cl	–	81[d]	4050	4050
12	**2c**	Et	–	10.8[e]	108	54

[a] Yield of epoxides to corresponding cyclic carbonates was determined by comparing the ratio of product to substrate in the ^{1}H NMR spectrum of an aliquot of the reaction mixture.
[b] Moles of cyclic carbonate produced per mole of catalyst.
[c] The rate is expressed in terms of the turnover frequency {TOF [mol of product (mol of catalyst h)$^{-1}$] = turnovers/h}.
[d] Reaction time 1 h.
[e] The equivalent (0.2%) NEt_3 was used as base.

From the results in Table 2, it is evident that the complexes bearing the *p*-dialklylamino substituent on the aryl ring (**2a–c**) are more efficient than the ligands bearing mesityl groups (**2d–f**) on the nitrogen atoms; **2c** here is most active catalyst, see Fig.1.

While comparing entry 3 with entry 7, it is clear that dichloromethane is not necessary as a solvent. This is an important phenomenon in green chemistry. In contrast to a reported study,[20] DMAP was a more active base with 71.1% yield (line

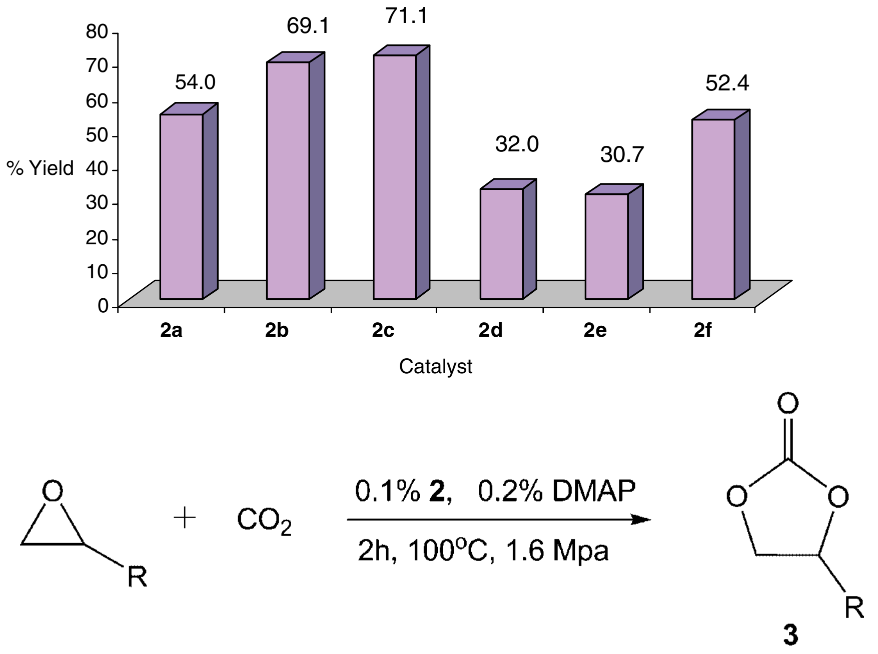


Figure 1. The formation of 1,2-epoxybutane to corresponding cyclic carbonate (4-ethyl-1,3-dioxolane-2-one) at the same catalytic conditions with **2c** catalyst.

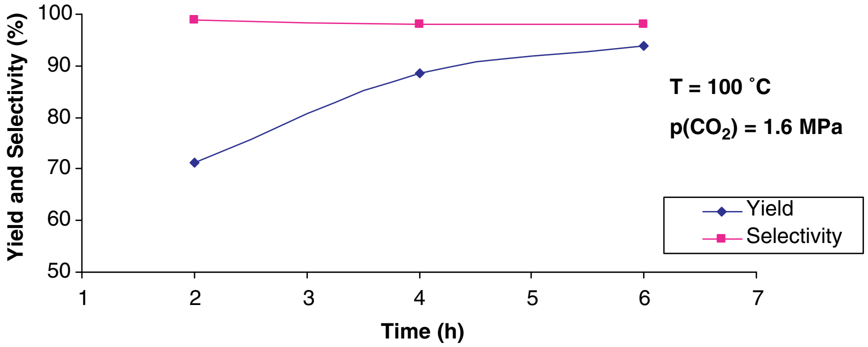


Figure 2. Conversion and selectivity of 1,2-epoxybutane as a function of time with **2c** catalyst.

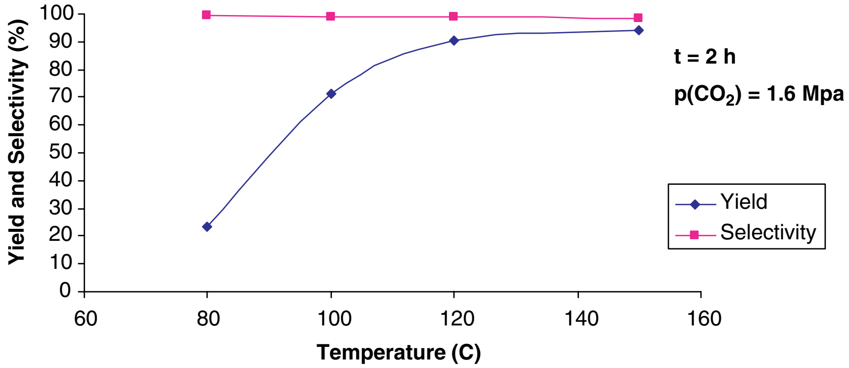


Figure 3. Conversion and selectivity of 1,2-epoxybutane as a function of temperature with **2c** catalyst.

3); the yield decreased to 10.8% when NEt_3 was replaced as a base (Table 2, line 12).

Regarding the reaction mechanism, we envisioned the occurrence of a similar pathway to that proposed previously,[14] i.e. activation of the epoxide by a Lewis acid and attacks of Lewis base (DMAP) on the sterically less hindered carbon atom to open the epoxide ring. The generated oxy anion species then react with CO_2 to give the cyclic carbonate.

Once the most efficient ruthenium complex had been identified (**2c**), the reaction conditions were evaluated, with a particular emphasis on reaction time, temperature and CO_2 pressure effects (Figs 2–4).

The reaction conditions such as reaction time, temperature and CO_2 pressure were shown to have an influence on the catalytic activity of transformation of EB to its related cyclic carbonate (see Figs 2–4) using **2c** as a catalyst. The EB reached 93.8% yield within 6 h, with CO_2 pressure 1.6 MPa at 100 °C (Fig. 2). The reaction rate increased with increasing temperature (Fig. 3), but interestingly, increasing CO_2 pressure above 1.6 MPa decreased the yield and turnover frequency (TOF) value (Fig. 4). A similar effect was reported by Darensbourg:[21] catalytic transformation of CO_2 to polycarbonate increased with increasing the pressure, but the value of TOF was decreased.

Cyclic voltammetric studies of Ru(II) complexes were performed in MeCN using a glassy-carbon working electrode, under anaerobic conditions over the potential range from −2.0 to +2.0 V vs Ag–AgCl at scan rate 0.1 or 0.25 V s^{-1}. Cyclic voltammogram of supporting electrolyte Bu_4NPF_6 in MeCN showed an absence of redox waves. A quasi-reversible ligand based reduction peak was observed in the range −1.02 to −1.34 V, which corresponds

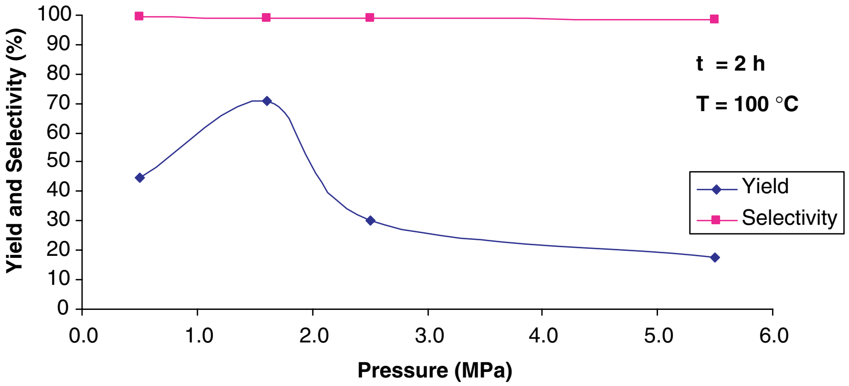


Figure 4. Conversion and selectivity of 1,2-epoxybutane as a function of pressure with **2c** catalyst.

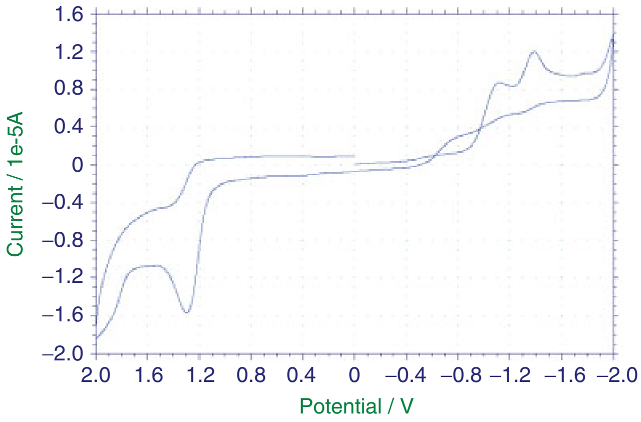


Figure 5. Cyclic voltammogram of **2c** complex in MeCN containing Bu_4NPF_6 as supporting electrolyte with scan rate = 0.25 V s^{-1}.

to reduction of the azomethine (CH=N) moiety of the Schiff base ligands.[22] The cyclic voltammograms of all the complexes displayed one quasi-reversible oxidation with $E_{1/2}$ values of 1.28–1.39 V. In general, the changes in oxidation and reduction potential were probably due to the relative stabilization of the ruthenium(II) state over ruthenium(III).

It was also observed from the electrochemical data that the most active catalyst (**2c**, bearing *p*-NEt_2 moiety on Schiff base) had the lowest oxidation potential (1.28 V), (Fig. 5) because of having more electron donating substituents on it. This indicates that more e-donating substituents lead to more efficient catalysts.

Conclusion

The new complexes **2**, synthesized in good yields, generate an active and useful catalyst for cycloaddition of CO_2 to epoxides in good to excellent yields. Important strengths of our protocol are: (i) low catalyst loading; and (ii) lower CO_2 pressure, which can be compared with those reported earlier.[14]

Experimental Section

General Considerations

Syntheses were performed under pure argon only for **2d–f** with rigorous exclusion of air and moisture using standard Schlenk techniques. All reagents were purchased from Aldrich and Merck. The solvents, Et_2O, pentane–hexane and toluene over Na and CH_2Cl_2 over P_2O_5 were distilled prior to use. ^1H and ^{13}C NMR spectra were recorded at 297 K using a Varian AS-400 spectrometer operating at 400 (^1H), 100.56 (^{13}C) and 376 MHz (^{19}F) in $CDCl_3$. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrometer as KBr pellets. Four of the starting Schiff bases (**1a**,[17a] **1b**,[17a] **1c**[17b] and **1d**[17c]) were prepared by known methods.

Synthesis of 1,3-bis(2,4,6-Trimethylphenylimino)propane (1e)

To a methanolic solution of 1,3-diaminoropane (0.84 ml, 10.0 mmol), mesitylaldehyde (2.95 ml, 20.0 mmol) was added drop wise. The off-white solid obtained at room temperature after 2–4 h was filtered off, and then crystallized from methylene chloride (5 ml) and methanol (8 ml). Yield 78%; m.p. 77 −81 °C. ^1H NMR (δ ppm) 2.16 (m, 2H, CH_2-CH_2-CH_2); 2.31 (s, 6H, C_6H_2-*p*-CH_3); 2.42 (s, 12H, C_6H_2-*o*-CH_3); 3.79 (t, 4H, J = 6.8, 7.2 Hz, CH=N-CH_2); 6.88 (s, 4H, C_6H_2); 8.64 (s, 2H, CH=N). ^{13}C NMR (δ ppm): 20.8; 21.3; 32.9; 60.5; 129.5; 131.6; 137.5; 138.8; 161.4 (CH=N).

Synthesis of 2,2′-Dimethyl-1,3-bis(2,4,6-trimethylphenylimino)propane (1f)

Compound **1f** was prepared in the same way as **1e** from 2,2′-dimethyl-1,3-diaminopropane (1.2 ml, 10.0 mmol) and mesitylaldehyde (2.95 ml, 20.0 mmol) to give off-white crystals. Yield 65%; m.p. 60–62 °C. ^1H NMR (δ ppm) 1.12 [s, 6H, CH_2-C-$(CH_3)_2$-CH_2]; 2.30 (s, 6H, C_6H_2-*p*-CH_3); 2.46 (s, 12H, C_6H_2-*o*-CH_3); 3.59 (s, 4H, -CH_2-CH_2-); 6.88 (s, 4H, C_6H_2); 8.64 (s, 2H, CH=N).[13]C NMR (δ ppm): 21.2; 21.3; 25.0; 36.8; 72.3; 129.7; 131.5; 137.8; 138.8; 161.5 (CH=N).

Synthesis of [Ru(1a)(*p*-cymene)Cl][BF_4] (2a)

To a methanolic solution of **1a** (0.162 g, 0.5 mmol) equimolar $NaBF_4$ (0.028 g, 0.025 mmol) and Ru-*p*-cymene (0.153 g, 0.025 mmol) were added. The color of mixture immediately turned from red to yellow-orange. The reaction mixture was stirred at room temperature for 2 h, then volatiles were evaporated in vacuum to dryness. The residue was dissolved in CH_2Cl_2 and filtered via a cannula on celite. The desired product was obtained after concentration of CH_2Cl_2 (3 ml) and then precipitating with diethyl ether (10 ml). The orange solid was obtained in 85% yield; m.p. 98–103 °C. ^1H NMR (δ ppm) 1.22 (m, 6H, cym-$CHCH_3$); 2.27 (s, 3H, cym-CH_3); 2.93 (m, 1H, cym-$CHCH_3$); 3.12 (m, 12H, C_6H_4-NCH_3); 3.51–4.08 (m, 4H, -NCH_2CH_2N-); 4.96 (d, J = 1.5 Hz, 2H, cym); 5.15 (d, J = 1.5 Hz, 2H, cym); 6.76 (d, J = 2.3 Hz, 4H, Ar); 8.20 (d, J = 2.3 Hz, 4H, Ar); 8.78 (s, 2H, N=CH). ^{13}C NMR (δ ppm): 18.3; 22.8; 30.7; 40.3; 65.0; 84.0; 85.8; 106.9; 111.2; 121.1; 133.3; 153.1; 174.9 (N=CH). ^{19}F NMR (δ): −57 510.6.

Synthesis of [Ru(1b)(p-cymene)Cl][BF_4] (2b)

Compound **2b** was prepared in the same way as **2a** from **1a** to give orange-yellow solid. Yield 82%; m.p. 162–165 °C. ^1H NMR (δ ppm): 1.29 (d, J = 1.7 Hz, 6H, cym-$CHCH_3$); 1.85 (m, 2H, -$NCH_2CH_2CH_2N$-); 2.07 (s, 3H, cym-CH_3); 2.31 (m, 1H, cym-$CHCH_3$); 2.98 (m, 2H, -$NCH_2CH_2CH_2N$-); 3.04 (m, 12H, C_6H_4-NCH_3); 3.74 (m, 2H, -$NCH_2CH_2CH_2N$-); 4.62 (d, J = 1.5 Hz, 1H, cym); 5.45 (d, J = 1.5 Hz, 1H, cym); 5.63 (d, J = 1.5 Hz, 1H, cym); 6.03 (d, J = 1.5 Hz, 1H, cym); 6.75 (m, 4H, Ar); 7.65 (d, J = 2.3 Hz, 2H, Ar); 8.24 (d, J = 2.3 Hz, 2H, Ar); 8.54 (s, 1H, N=CH); 8.78 (s, 1H, N=CH′). ^{13}C NMR (δ ppm): 18.7; 212; 25.9; 30.5; 40.3; 54.8; 63.8; 68.2; 85.3; 86.8; 100.7; 105.4; 111.1; 111.4; 119.9; 120.8; 133.8; 133.9; 152.7; 152.9; 173.9 (N=CH); 174.6 (N=C′H). ^{19}F NMR (δ ppm): −57 589.7.

Synthesis of [Ru(1c)(p-cymene)Cl][BF_4] (2c)

Compound **2c** was prepared in the same way as **2a** from **1c** to give orange-yellow solid. Yield 75%; m.p. 131–134 °C. ^1H NMR (δ ppm): 1.23 (m, 12H, C_6H_4-NCH_2CH_3); 1.71 (s, 6H, cym-$CHCH_3$); 2.19 (s, 3H, cym-CH_3); 2.85 (m, 1H, cym-$CHCH_3$); 3.39 (m, 8H, C_6H_4-NCH_2CH_3); 4.04 (m, 4H, -NCH_2CH_2N-); 5.02 (d, J = 1.5 Hz, 2H, cym); 5.14 (d, J = 1.5 Hz, 2H, cym); 8.12–8.19 (m, 8H, Ar); 8.67 (s, 2H, N=CH).[13]C NMR (δ ppm) : 12.7; 18.4; 22.9; 30.8; 44.8; 65.2; 84.0; 85.9; 100.5; 107.0; 110.8; 120.3; 133.7; 134.2; 174.7 (N=CH). ^{19}F NMR (δ ppm) : −57 468.6.

Synthesis of [Ru(1d)(p-cymene)Cl][BF_4] (2d)

To a freshly distilled THF solution of Ru-*p*-cymene (0.153 g, 0.025 mmol) under argon **1a** (0.160 g, 0.5 mmol) and equimolar $NaBF_4$ (0.028 g, 0.025 mmol) was added. The mixture was stirred for 3 h at room temperature. The volatiles were evaporated in vacuum to dryness. Residue was dissolved with CH_2Cl_2 and filtered via cannula on celite. The desired product was obtained after concentration of CH_2Cl_2 (3 ml) and then precipitating with diethyl ether (10 ml). The air and moisture stable pale yellow solid was obtained in 75% yield; m.p. 278–281 °C. ^1H NMR (δ ppm): 1.10 (d, $J = 7.2$ Hz, 3H, cym-CHCH_3); 1.20 (d, $J = 6.8$ Hz, 3H, cym-CHCH'_3); 2.08 (s, 3H, C_6H_2-*o*-CH_3); 2.17 (s, 3H, C_6H_2-*o*-CH_3); 2.23 (s, 3H, C_6H_2-*o*-$CH_{3'}$); 2.29 (s, 3H, C_6H_2-*p*-CH_3); 2.30 (s, 3H, C_6H_2-*p*-CH''_3); 2.34 (s, 3H, C_6H_2-*o*-CH'''_3); 2.47 (s, 3H, C_6H_4-*p*-CH'_3); 2.66 [m, 1H, cym-CH-$(CH_3)_2$]; 3.26 (m, 1H, -CH_2-CH_2-); 3.53–3.49 (dd, $J = 5.2$, 4.4 Hz, 1H, -$CH_{2'}$-CH_2-); 3.68 (m, 1H, -CH_2-CH_2-); 3.93–3.94 (dd, $J = 4.8$, 5.2 Hz, 1H, -CH_2-$CH_{2'}$-); 4.35 (d, $J = 5.6$ Hz, 1H, cym); 4.81 (d, $J = 5.2$ Hz, 1H, cym); 5.06 (d, $J = 6.4$ Hz, 1H, cym); 5.13 (d, $J = 6.4$ Hz, 1H, cym); 6.81 (s, 1H, C_6H_2-*m*-CH); 6.88 (s, 1H, C_6H_2-*m*-CH'); 6.94 (s, 1H, C_6H_2-*m*-CH''); 6.98 (s, 1H, C_6H_2-*m*-CH'''); 8.97 (s, 1H, -CH=N); 9.10 (sl, 1H, -CH'=N). ^{13}C NMR (δ ppm): 18.7; 19.7; 20.1; 20.2; 20.7; 21.3; 21.4; 21.5; 31.0; 56.6; 63.2; 80.0; 86.0; 128.7; 129.3; 129.4; 130.3; 134.2; 135.3; 135.9; 136.1; 136.4; 140.4; 140.8; 179.2 (N=CH); 179.8 (N=C' H).[19]F NMR (δ ppm): (d, $J = 16.8$ Hz); 42 446.1.

Synthesis of [Ru(1e)(*p*-cymene)Cl][BF_4] (2e)

Compound **2e** was prepared in the same way as **2d** from **1e** to give yellow solid. Yield 72%; m.p. 191–195 °C. ^1H NMR (δ ppm): 1.16 (d, $J = 6.8$ Hz, 3H, cym-CH_3); 1.25 (d, $J = 7.2$ Hz, 6H, C_6H_2-*p*-CH_3); 2.13 (s, 3H, C_6H_2-*o*-CH_3); 2.16 (s, 3H, C_6H_2-*o*-CH'_3); 2.31 (s, 3H, C_6H_2-*o*-CH''_3); 2.36 (s, 3H, C_6H_2-*o*-CH'''_3); 2.42 (s, 3H, cym-CHCH_3); 2.45 (s, 3H, cym-CHCH'_3); 2.59 (m, 2H, -CH_2-CH_2-CH_2-); 2.81 (m, 1H, cym-CH-$(CH_3)_2$); 3.65 (m, 1H, -CH_2-CH_2-CH_2-); 3.79 (m, 1H, -$CH'_{2'}$-CH_2-CH_2-); 3.91 (m, 1H, -$CH_{2'}$-CH_2-CH_2-); 4.11 (m, 1H, -$CH_{2'}$-CH_2-$CH_{2'}$-); 4.72 (d, $J = 6$ Hz, 1H, cym); 4.97 (d, $J = 6.4$ Hz, 1H, cym); 5.09 (d, 6 Hz, 1H, cym); 5.19 (d, $J = 5.6$ Hz, 1H, cym); 6.86 (s, 1H, C_6H_2-*m*-CH); 6.96 (s, 1H, C_6H_2-*m*-CH'); 6.99 (s, 1H, C_6H_2-*m*-CH''); 7.05 (s, 1H, C_6H_2-*m*-CH'''); 8.90 (s, 1H, -CH=N); 9.24 (s, 1H, -CH'=N).[13]C NMR (δ ppm): 18.7; 19.5; 20.3; 20.4; 20.9; 21.3; 21.5; 22.8; 26.6; 31.3; 52.8; 62.5; 128.7; 129.0; 129.3; 129.5; 133.0; 134.4; 135.2; 135.3; 136.4; 140.5; 141.3; 178.9 (N=CH); 182.5 (N=C' H).[19]F NMR (δ ppm): (d, $J = 19.8$ Hz); 42 478.2.

Synthesis of [Ru(1f)(*p*-cymene)Cl[BF_4]] (2f)

Compound **2f** was prepared in the same way as **2d** from **1f** to give yellow solid. Yield 70%; m.p. 94–98 °C. ^1H NMR (δ ppm): 0.39 [s, 3H, -CH_2-C$(CH_3)_2$-CH_2-]; 0.45 [s, 3H, -CH_2-C$(CH'_3)_2$-CH_2-]; 1.04 (d, $J = 6$ Hz, 3H, cym-CH_3); 1.30 (d, J = 6.8 Hz, 6H, C_6H_2-*p*-CH_3); 2.16 (s, 3H, C_6H_2-*o*-CH_3); 2.18 (s, 3H, C_6H_2-*o*-CH'_3); 2.21 (s, 3H, C_6H_2-*o*-CH''_3); 2.39 (s, 3H, C_6H_2-*o*-CH'''_3); 2.47 (s, 3H, cym-CHCH_3); 2.57 (s, 3H, cym-CHCH'_3); 2.78 (m, 1H, cym-CH-$(CH_3)_2$); 2.81 [m, 2H, -CH_2-C$(CH_3)_2$-CH_2-]; 3.65 (m, 2H, -CH_2-C$(CH_3)_2$-CH_2-); 5.04 (d, $J = 6.4$ Hz, 1H, cym); 5.33 (d, $J = 5.6$ Hz, 1H, cym); 5.63 (d, $J = 6.4$ Hz, 1H, cym); 5.94 (d, $J = 6$ Hz, 1H, cym); 6.86 (s, 1H, C_6H_2-*m*-CH); 6.95 (s, 2H, C_6H_2-*m*-CH'); 7.04 (s, 1H, C_6H_2-*m*-CH''); 8.86 (s, 1H, -CH=N); 9.24 (s, 1H, -CH'=N)^{13}C NMR (δ ppm): 18.8; 19.1; 19.7; 20.6; 20.7; 21.7; 22.4; 22.6; 23.7; 24.2; 26.9; 31.0; 35.1; 55.3; 65.0; 128.9; 129.0; 129.6; 129.8; 129.9; 130.2; 130.7; 133.6; 137.3; 137.8; 140.8; 141.7; 144.0; 180.6(N=CH); 193.2 (N=C' H). ^{19}F NMR (δ ppm): (d, $J = 19.8$ Hz); 42 923.7.

General Procedure for the Cycloaddition of Epoxides to CO_2

A 50 ml stainless pressure reactor was charged with complex **2** (4.5×10^{-5} mol), epoxide (4.5×10^{-2} mol), DMAP (11 mg, 9.0×10^{-5} mol) or Net_3 (0.013 ml, 9.0×10^{-5} mol), using CH_2Cl_2 (5.0 ml). The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate and CO_2 was charged into the autoclave with the desired pressure then heated to the desired temperature. The pressure was kept constant during the reaction. The vessel was then cooled to 5–10 °C in ice bath after the desired reaction time. The pressure was released, then the excess gases were vented. The yields of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.

Acknowledgment

The authors are grateful to TÜBİTAK (106T364) for research funds and for support.

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