Coordination Chemistry

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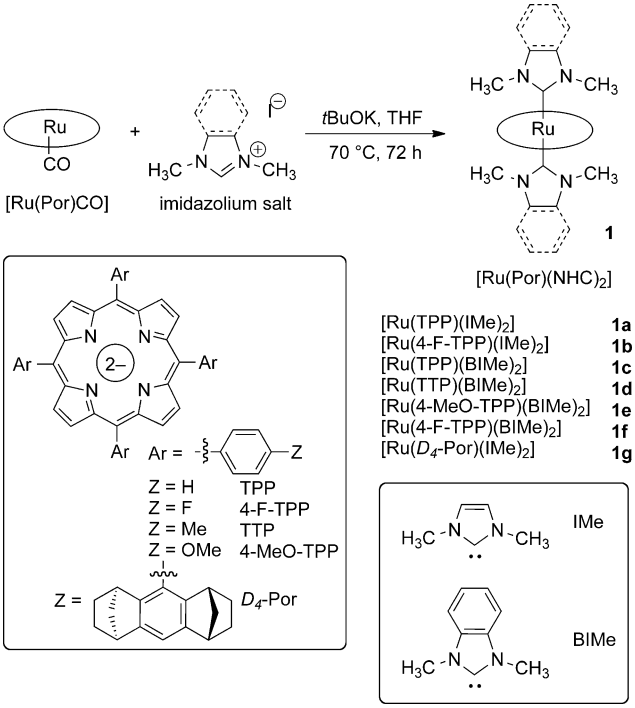
Elevated Catalytic Activity of Ruthenium(II)–Porphyrin-Catalyzed Carbene/Nitrene Transfer and Insertion Reactions with N-Heterocyclic Carbene Ligands**

Ka-Ho Chan, Xiangguo Guan, Vanessa Kar-Yan Lo, and Chi-Ming Che**

Abstract: *Bis(NHC)ruthenium(II)–porphyrin complexes were designed, synthesized, and characterized. Owing to the strong donor strength of axial NHC ligands in stabilizing the trans M=CRR′/M=NR moiety, these complexes showed unprecedently high catalytic activity towards alkene cyclopropanation, carbene C–H, N–H, S–H, and O–H insertion, alkene aziridination, and nitrene C–H insertion with turnover frequencies up to 1950 min^{-1}. The use of chiral [Ru(D_4-Por)(BIMe)$_2$] (**1g**) as a catalyst led to highly enantioselective carbene/nitrene transfer and insertion reactions with up to 98% ee. Carbene modification of the N terminus of peptides at 37°C was possible. DFT calculations revealed that the trans axial NHC ligand facilitates the decomposition of diazo compounds by stabilizing the metal–carbene reaction intermediate.*

Metal-catalyzed carbene/nitrene transfer to C=C bonds[1] and insertion into X–H bonds (in which X = C, N, O)[1c,d,f,2] are important tools in organic synthesis. Reactive metal–carbene[1c–f,2,3] or metal–nitrene[1g,2d,e] species are widely perceived to be the key intermediates. In this regard, the stability and reactivity of the metal–carbene or metal–nitrene intermediates is crucial, as mild reaction conditions are beneficial to asymmetric catalysis and bioconjugation reactions. The axial ligand *trans* to the M=CRR′/M=NR moiety can significantly alter the reactivity of the latter.[2e] We have reported that [Os(F_{20}-TPP)(CPh_2)$_2$] (H_2F_{20}-TPP = *meso*-tetrakis(pentafluorophenyl)porphyrin) readily undergoes alkene cyclopropanation and C–H functionalization, in contrast to its inert monocarbene counterpart, thus revealing the significance of the *trans* Ph_2C ligand in elevating the reactivity of the Os=CPh_2 moiety towards carbene transfer and insertion reactions.[4]

N-Heterocyclic carbene (NHC) ligands are increasingly used in transition-metal catalysis.[5] The strong σ-donor character of NHCs is reminiscent of that of an Ar_2C ligand and holds promise in elevating the reactivity of the *trans*-metal-carbene/metal-nitrene unit. In this study, the [Ru(Por)(NHC)$_2$] complexes **1a–g** (Scheme 1) were found to display high catalytic activity towards alkene cyclopropanation, carbene X–H insertion (X = C, N, S, O), alkene aziridination, and nitrene C–H insertion with turnover frequencies up to 1950 min^{-1}. The use of chiral [Ru(D_4-Por)(BIMe)$_2$] (**1g**; D_4 refers to the symmetry of the ligand) as the catalyst led to highly enantioselective carbene/nitrene transfer and insertion reactions with up to 98% *ee*. Carbene modification of the N terminus of a peptide at 37°C was possible. DFT calculations revealed that the *trans* axial NHC ligand stabilizes the metal–carbene intermediate formed by the decomposition of diazo compounds.



Scheme 1. Synthesis of [Ru(Por)(NHC)$_2$] complexes.

[Ru(Por)(NHC)$_2$] complexes **1a–g** were synthesized by treating [Ru(Por)CO] (1 mmol) with the corresponding imidazolium salt (12 mmol) and *t*BuOK (10 mmol) in THF (60 mL) at 70°C for 72 h. These complexes are soluble in

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common organic solvents and are stable in the open atmosphere in solution (for at least 1 week in $CDCl_3$) and in the solid state (for at least 1 month), as revealed by ^{1}H NMR spectroscopy and ESIMS analysis. The X-ray crystal structure of **1b** revealed that the axially coordinated NHC ligands are roughly orthogonal to the porphyrin plane (Figure 1).[6] The

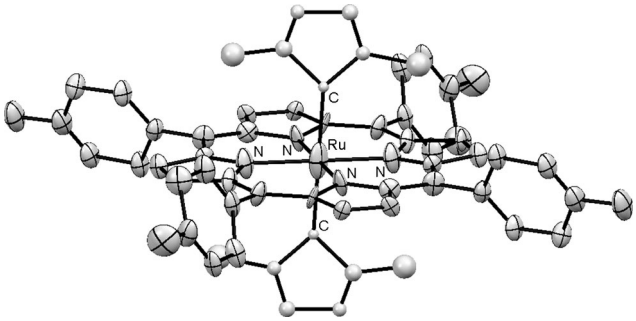


Figure 1. Perspective view of [Ru(4-F-TPP)(IMe)$_2$] (**1b**). Hydrogen atoms are omitted for clarity. Non-hydrogen atoms are represented by thermal ellipsoids drawn at the 30% probability level.

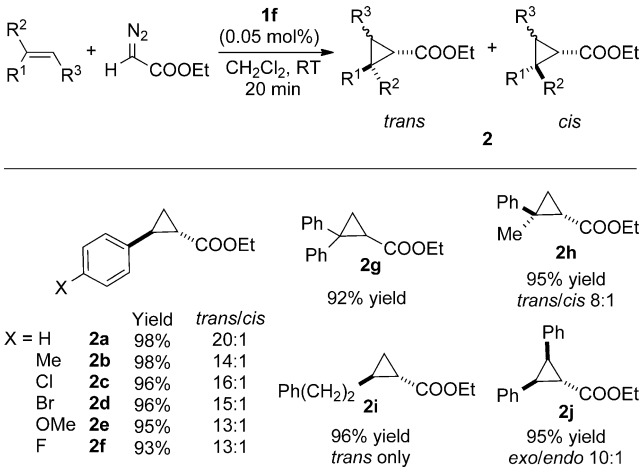
Ru–C(NHC) distances are both 2.076 Å and thus comparable to those reported for Ru–C single bonds (2.07–2.15 Å for Ru–C(NHC)).[7]

As representative examples, the conversion of [Ru(4-F-TPP)CO] into **1b** (Scheme 1) led to a red shift of the Soret band and a blue shift of the β band (see Figure S1 in the Supporting Information). The ^{13}C NMR spectra of **1a**–**1g** all showed (Ru–C) signals at $\delta = 140$–150 ppm.[1d,7] The IR oxidation-state marker bands of **1a**–**g** all fell into the range of 998–1005 cm^{-1}, consistent with the Ru^{II} oxidation state.[8]

The electrochemistry of complexes **1a**–**f** and [Ru(Por)CO] was examined. The first oxidation couple of [Ru(Por)(NHC)$_2$] is much less anodic as compared to that of [Ru(Por)CO] (see Table S1 in the Supporting Information). For example, in the case of **1b** and [Ru(4-F-TPP)CO], the oxidation couple of **1b** at $E_{1/2} = -0.04$ V (with reference to Ag/AgNO$_3$ (0.1 M in CH$_3$CN)) was less anodic by 660 mV than that of [Ru(4-F-TPP)CO] ($E_{1/2} = 0.70$ V; see Figure S2). This change is attributed to the oxidation of Ru^{II} to Ru^{III}. The remarkably low $E_{1/2}$ value reflects substantial stabilization of the Ru^{III} species by the two strong σ-donor NHC ligands. The second oxidation couple was tentatively assigned to porphyrin-centered oxidation.

To evaluate the catalytic activity of the [Ru(Por)(NHC)$_2$] complexes, we examined the cyclopropanation of styrene with ethyl diazoacetate (EDA; see Table S2). A solution of EDA (0.8 mmol) in CH_2Cl_2 was added to a mixture of styrene (1.6 mmol) and the catalyst (0.05 mol%) in CH_2Cl_2 at room temperature under a N_2 atmosphere over a period of 10 min by the use of a syringe pump. The mixture was then stirred for a further 10 min at room temperature. The best result was obtained by using [Ru(4-F-TPP)(BIMe)$_2$] **1f** as the catalyst, which led to the formation of **2a** in 98% yield with a *trans*/*cis* ratio of 20:1 (Scheme 2; see Table S2). As compared to [Ru(TPP)CO] (slow addition of EDA over 8 h plus additional stirring for 8 h led to the product in 65% yield; see Table S2), [Ru(Por)(NHC)$_2$] complexes showed significantly higher reactivity towards alkene cyclopropanation. Lowering of the catalyst loading of **1f** to 0.004 mol% led to complete EDA consumption within 20 min with the formation of cyclopropane **2a** in 78% yield (see Table S2), thus indicating a turnover frequency of 1950 min^{-1}.

We examined other alkenes (Scheme 2) and found that the catalytic cyclopropanation reaction proceeded smoothly for styrenes bearing electron-donating (*p*-Me and *p*-OMe)

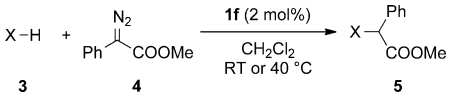


Scheme 2. Alkene cyclopropanation with EDA under the catalysis of **1f**. Reaction conditions: alkene (1.6 mmol), EDA (0.8 mmol), **1f** (0.05 mol%), CH_2Cl_2 (2 mL). The yields given are for the isolated product (as based on EDA). The *trans*/*cis* and *exo*/*endo* ratios were determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

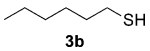
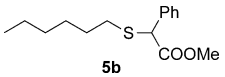
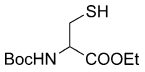
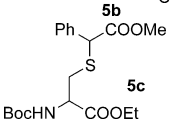
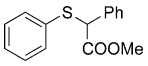
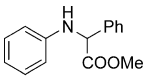
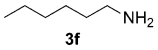
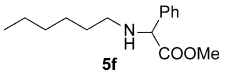
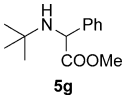
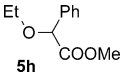
and electron-withdrawing (*p*-Cl, *p*-Br, and *p*-F) substituents: Cyclopropanes **2b**–**f** were obtained in 93–98% yield with excellent selectivity. Reactions of *gem*-disubstituted alkenes proceeded smoothly to give **2g** and **2h**. Cyclopropanation of aliphatic 4-phenyl-1-butene with EDA gave exclusively *trans*-**2i**, which was isolated in 96% yield. *cis*-Stilbene also underwent cyclopropanation smoothly with EDA to give **2j** in 95% yield with an *exo*/*endo* ratio of 10:1. In all reactions in Scheme 2, EDA was completely consumed in 20 min, and no EDA coupling product was detected.

We further expanded our study to carbene C–H insertion (Table 1). The reaction of 1,4-cyclohexadiene (**3a**; 4 mmol), methyl phenyldiazoacetate (**4**; 0.4 mmol), and **1f** (2 mol%) in CH_2Cl_2 (2 mL) at reflux for 24 h afforded **5a**, the product of insertion into a vinyl C–H bond, in 81% yield (Table 1, entry 1). The reaction also proceeded under neat conditions to give **5a** in 78% yield (Table 1, entry 1). No carbene dimer or cyclopropane was detected in the crude product mixture, and the diazo compound **4** was even added in one portion. In contrast, [Ru(TPP)CO] was inactive towards this reaction under the same reaction conditions. We compared other metalloporphyrin catalysts (see Table S3) and found that the catalytic activity of **1f** was superior to that of a range of Ru^{II}, Fe^{III}, Co^{II}, and Mn^{III} metalloporphyrin catalysts, all of which are well-documented to be effective in catalyzing carbene

Table 1: Carbene X–H insertion reactions catalyzed by **1f**.[a]



3 4 5

Entry	3	Reaction conditions	Product	Yield [%][b]
1	 **3a**	24 h, 40 °C	 **5a**	81 (78)
2	 **3b**	12 h, 40 °C	 **5b**	97
3	 **3c**	12 h, RT	 **5c**	78
4	 **3d**	8 h, RT	 **5d**	98
5	 **3e**	4 h, RT	 **5e**	98
6	 **3f**	12 h, 40 °C	 **5f**	95
7	 **3g**	8 h, RT	 **5g**	95
8	EtOH **3h**	12 h, 40 °C	 **5h**	55 (70)

[a] Reaction conditions: **3** (4 mmol), **4** (0.4 mmol), **1f** (2 mol%), CH_2Cl_2 (4 mL). [b] Yield of the isolated product (as based on EDA); the yields (isolated product) in parentheses are for the reaction performed under neat conditions. Boc = *tert*-butoxycarbonyl.

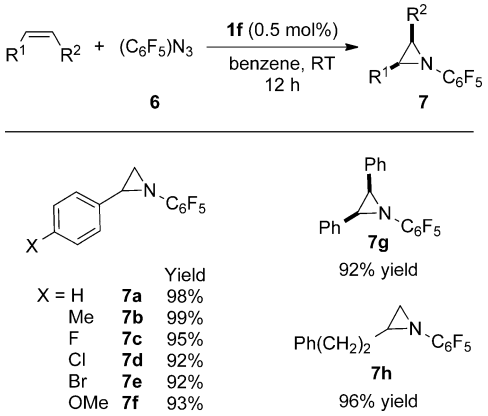
transfer reactions.[1b,d–f,2d,e,3] This finding shows that the incorporation of the axially coordinated NHC ligands highly facilitates carbene transfer and insertion reactions.

Complex **1f** is also catalytically active towards carbene insertion into S–H, N–H, and O–H bonds. Aliphatic 1-hexanethiol (**3b**), protected cysteine **3c**, and thiophenol (**3d**) underwent carbene S–H insertion with **4** to give **5b–d** in 97, 78, and 98% yield, respectively (Table 1, entries 2–4). Carbene N–H insertion of aniline (**3e**), aliphatic hexaylamine (**3f**), and *tert*-butylamine (**3g**) was completed in 4–12 h to give **5e–g** in 95–98% yield (Table 1, entries 5–7). Carbene O–H insertion of EtOH (**3h**) at 40 °C led to **5h** in 55% yield in 12 h (Table 1, entry 8). The yield of **5h** was boosted to 70% when the reaction was performed under neat conditions (Table 1, entry 8).

We further extended our study to alkene aziridination (Scheme 3). When alkenes (0.6 mmol) were treated with pentafluorophenyl azide (**6**; 0.5 mmol) and **1f** (0.5 mol%) in benzene for 12 h at room temperature under a N_2 atmosphere, aziridines **7a–h** were obtained in 92–99% yield. To the best of our knowledge, there are few examples of alkene aziridination with aryl azides as the nitrene source under such mild conditions.[9]

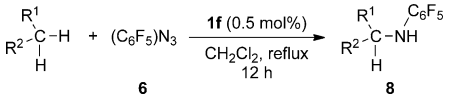
Nitrene insertion into saturated C–H bonds with **6** was also catalyzed by **1f** (Table 2). When a solution of **6** (0.5 mmol), a hydrocarbon (5 mmol), and **1f** (0.5 mol%) in CH_2Cl_2 was heated at reflux for 12 h under a N_2 atmosphere, **6** was completely consumed according to TLC analysis, and amines **8a–h** were isolated in 88–96% yield (Table 2, entries 1–8). The nitrene C–H insertion proceeded well with the unactivated C–H bonds of cyclohexane and primary C–H bonds of toluene to give **8a** and **8c** in 90 and 92% yield, respectively (Table 2, entries 1 and 3).

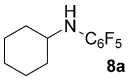
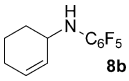
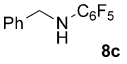
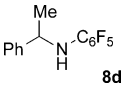
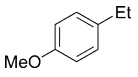
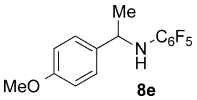
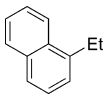
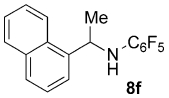
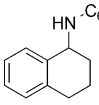
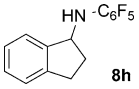
The chiral [Ru(Por)$(NHC)_2$] catalyst **1g** was prepared for asymmetric reactions (Scheme 4). Under the conditions depicted in Scheme 2, *trans*-(1*S*,2*S*)-cyclopropane **2a** was obtained in 98% yield with 95% *ee* in 40 min at room temperature [Eq. (1)]. Lowering of the catalyst loading to 0.004 mol% led to complete consumption of EDA in 2 h and the formation of *trans*-(1*S*,2*S*)-**2a** in 95% yield with 95% *ee*, thus revealing a turnover number of 23750. The reaction of **3a** and **4** in the presence of **1g** (2 mol%) led to (*R*)-**5a** in 80% yield with 92% *ee* [Eq. (2)]. The asymmetric aziridination of styrene and 4-phenyl-1-butene with **6** as the nitrene source proceeded smoothly in the presence of **1g** (0.5 mol%) at −20 °C for a period of 20 h to give (*R*)-**7a** and



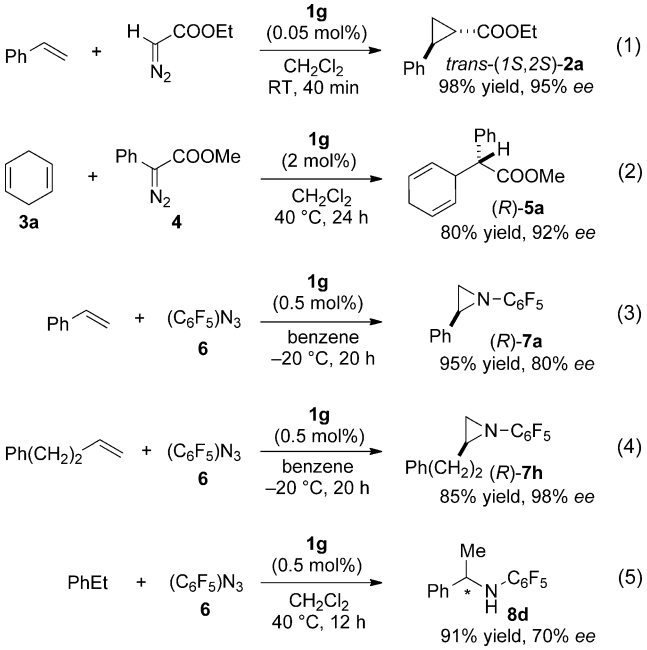
Scheme 3. Alkene aziridination with pentafluorophenyl azide (**6**) under the catalysis of **1f**. Reaction conditions: alkene (0.6 mmol), **6** (0.5 mmol), **1f** (0.5 mol%), benzene (2 mL). The yields given are for the isolated product.

Table 2: Nitrene insertion into saturated C–H bonds with pentafluorophenyl azide (**6**) under the catalysis of **1f**.[a]



Entry	Substrate	Product	Yield [%][b]
1	cyclohexane	 **8a**	90
2	cyclohexene	 **8b**	96
3	PhMe	 **8c**	92
4	PhEt	 **8d**	92
5		 **8e**	88
6		 **8f**	93
7		 **8g**	96
8		 **8h**	93

[a] Reaction conditions: hydrocarbon (5 mmol), **6** (0.5 mmol), **1f** (0.5 mol%), CH_2Cl_2 (2 mL). [b] Yield of the isolated product.

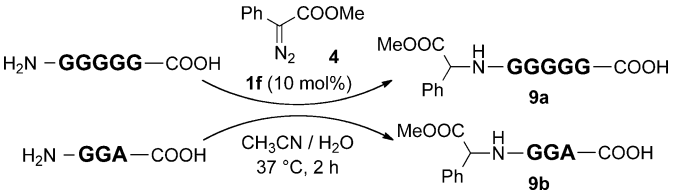


Scheme 4. Enantioselective carbene/nitrene transfer and insertion reactions catalyzed by **1g**.

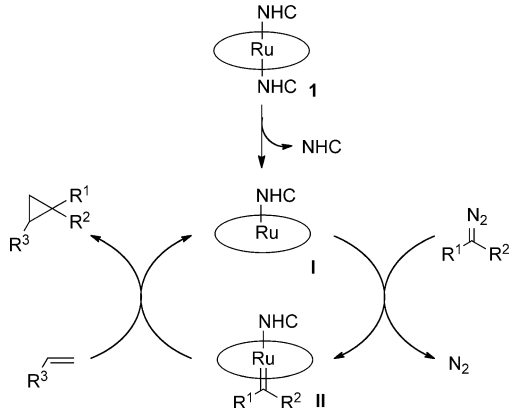
(*R*)-**7h** in 95% yield with 80% *ee* and 85% yield with 98% *ee*, respectively [Eqs. (3) and (4)]. Under the conditions depicted in Table 2, the asymmetric amination reaction of ethylbenzene and **6** in the presence of **1g** (0.5 mol%) gave amine **8d** in 91% yield with 70% *ee* [Eq. (5)].

As selective carbene S–H, N–H, and O–H bond insertion reactions are useful for the modification of biomolecules that have to be treated under mild conditions,[1d,2e,10] we modified the N terminus of peptides GGGGG and GGA through carbene N–H insertion with **1f** as the catalyst. When the peptides (1 mM) were stirred with **4** (10 equiv in dioxane) in an aqueous solution containing **1f** (10 mol%) at 37 °C for 2–3 h, **9a** and **9b** were obtained with complete substrate conversion (Scheme 5), as revealed by liquid chromatography–tandem mass spectrometry (LC–MS/MS; see Figures S3 and S4).

To gain insight into the reaction mechanism depicted in Scheme 6, we prepared the mono(NHC)ruthenium complex



Scheme 5. Carbene N-terminus modification of peptides



Scheme 6. Tentative reaction mechanism for carbene transfer or insertion.

10 with a THF molecule coordinated *trans* to the NHC ligand by the recrystallization of **1a** from THF. The X-ray crystal structure of **10** revealed that the Ru–C(NHC) distance was slightly shorter than that in **1b** (2.001 versus 2.076 Å in **1b**; see Figure S5).[6] Complex **10** displayed similar catalytic activity to that of **1a** in the cyclopropanation of styrene with EDA, thereby supporting the involvement of **I** in the mechanism.[11] The free NHC ligand is inactive towards the cyclopropantion of styrene with EDA, thus excluding its role as a catalyst.

We undertook DFT calculations with the Gaussian 09 package[12] at the M06L[13]/6-31G* (SDD for Ru) level for

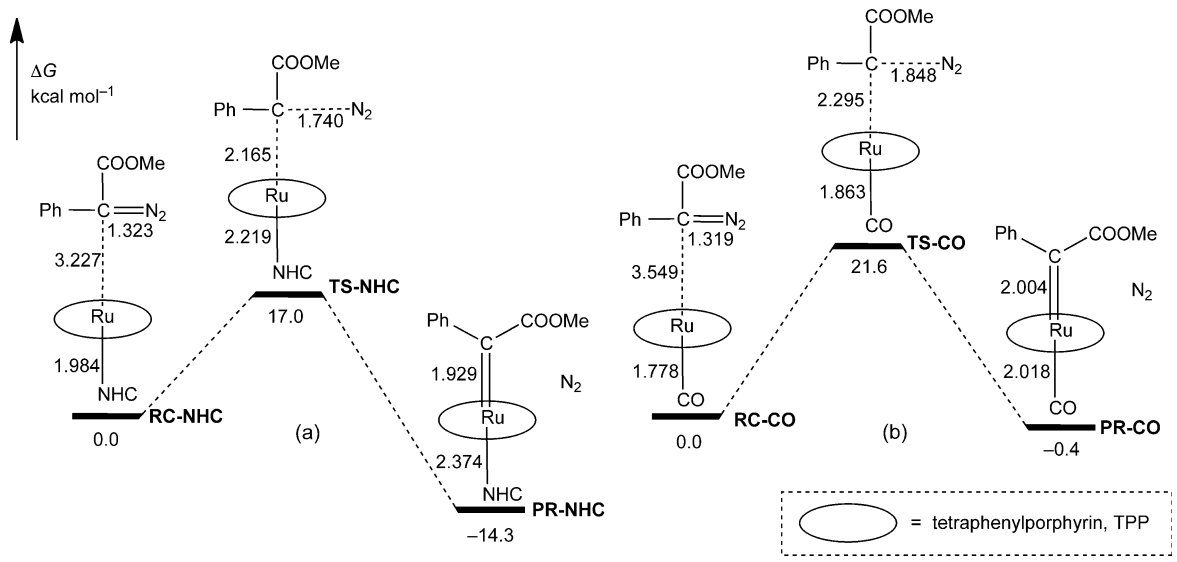


Figure 2. Calculated potential-energy surfaces for the formation of ruthenium–carbene intermediates with a) [Ru(TPP)(NHC)] (NHC = IMe) and b) [Ru(TPP)CO] at the M06L/6-311G*:SDD level.

geometry optimization and at the M06 L/6-311G* (SDD for Ru)[14] level for single-point energy correction to gain insight into the elevated catalytic activity of $[Ru(Por)(NHC)_2]$ complexes. Alkene cyclopropanation and insertion were studied as examples, and comparisons were made with similar reactions catalyzed by [Ru(Por)CO]. The free-energy profiles (with the correction of solvent effects) for the formation of $[Ru(TPP)(\mathbf{L})(CPh(CO_2Me))]$ ($\mathbf{L}$ = NHC, CO) intermediates are depicted in Figure 2.

In the formation of $[Ru(TPP)(L)(CPh(CO_2Me))]$, the decomposition of **4** by [Ru(TPP)(NHC)]: 1) features a much lower activation energy (17.0 versus 21.6 kcal mol^{-1}), 2) is more exothermic (−14.3 versus −0.4 kcal mol^{-1}), and 3) shows a significantly less elongated Ru–C(CPh(CO_2Me)) bond in the transition state (Ru···C distance: 2.165 (**TS-NHC**) versus 2.295 Å (**TS-CO**)) when compared with decomposition of **4** by the [Ru(TPP)CO] counterpart (Figure 2). The reaction involving [Ru(TPP)(NHC)] has an early transition state with a lower energy barrier as compared to the reaction catalyzed by [Ru(TPP)(CO)]. The difference in the reactivity is due to the *trans* ligand effect. The *trans* NHC ligand is a σ donor and hence stabilizes the Ru=CPh(CO_2Me) unit with a stronger bonding interaction than that formed with the *trans* CO ligand. This difference is also reflected by the calculated Ru–CPh(CO_2Me) distances (Ru···C distance: 1.929 (**PR-NHC**) versus 2.004 Å (**PR-CO**)). The decomposition of diazo compounds is usually rate-determining (RD) in metal-catalyzed carbene transfer and insertion reactions with diazo compounds as the carbene source.[15] Similarly, the high reactivity of $[Ru(Por)(NHC)_2]$ towards alkene aziridination by aryl azides (RN_3) could be attributed to the stabilization of the reactive [Ru(Por)(NHC)(NR)] intermediate owing to a strong NHC–Ru–NR interaction.

In conclusion, a series of $[Ru(Por)(NHC)_2]$ complexes were found to display unprecedentedly high catalytic activity towards carbene/nitrene transfer and insertion. The strong σ-donor strength of the *trans* NHC ligand leads to a lower activation barrier for the decomposition of diazo compounds and aryl azides, which is crucial for the metal-catalyzed oxidative C–C and C–N bond-forming reactions to proceed under mild reaction conditions.

Experimental Section

Synthesis of $[Ru(Por)(NHC)_2]$ complexes **1a**–**g**: A solution of the imidazolium salt (10 mmol), *t*BuOK (10 mmol), and [Ru(Por)CO] (1 mmol) in THF (60 mL) was heated at reflux under a N_2 atmosphere for 72 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and redissolved in hexane. Impurities were then filtered off. Recrystallization from benzene/pentane gave the desired complexes as brick-red crystals.

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