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C–H Activation

Highly Selective Metal Catalysts for Intermolecular Carbenoid Insertion into Primary C–H Bonds and Enantioselective C–C Bond Formation**

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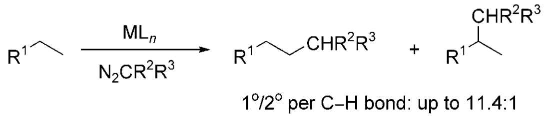
Direct functionalization of C–H bonds is an appealing strategy in organic synthesis[1] but its practical application has so far been difficult to realize. The selective functionalization of primary C–H bonds of alkanes that also contain secondary and/or tertiary C–H bonds is a great challenge, as C–H bond energy follows an order primary > secondary > tertiary.[1c,d] In seminal works by Bergman,[1b] Jones,[1c] and their respective co-workers, stoichiometric reactions of alkanes with $[Cp^*(Me_3P)M]$ ($Cp^* = C_5Me_5$; M = Rh, Ir) resulted in the formation of C–M bonds by selective activation of primary C–H bonds. Subsequent work by Hartwig and co-workers[1g,i,2] demonstrated C–B bond formation by stoichiometric and catalytic functionalization of primary C–H bonds mediated by tungsten, rhodium, or ruthenium complexes. The high selectivity for primary C–H bond functionalization in these C–M or C–B bond-formation reactions (Scheme S1 in the Supporting Information) is considered to result from kinetic factors or steric interaction between the metal complexes and alkanes.[1i,3]

A well-established process in C–C bond formation by direct C–H bond functionalization is the metal-catalyzed intra- and intermolecular carbenoid insertion into C–H bonds, with diazo compounds as the carbene source.[1o,4] These catalytic C–C bond-formation reactions generally feature lower selectivity for primary C–H bonds than for secondary and tertiary C–H bonds. For example, a selectivity order of primary < secondary < tertiary C–H bonds has been observed for the extensively investigated carbene insertion catalyzed by rhodium complexes,[4,5] possibly because of the electron density order of primary < secondary < tertiary C–H bonds, which renders primary C–H bonds the least susceptible to attack by electrophilic rhodium–carbene intermediates.[5] By manipulating the steric or electronic properties of the metal catalysts, a selectivity for primary C–H bonds of alkanes comparable to that for secondary or tertiary C–H bonds was observed,[6] with the highest primary/secondary and primary/tertiary ratio per C–H bond being 1.17:1.0[6b] and 1.0:0.9,[6c] respectively.

Herein we report a highly selective primary C–H bond functionalization by metal-catalyzed carbenoid insertion into the C–H bonds of alkanes (Scheme 1), which features a primary/secondary selectivity (that is, the primary/secondary ratio per C–H bond) of up to 11.4:1. We have also accomplished highly enantioselective functionalization of secondary C–H bonds with *ee* values of up to 93% and product turnovers up to 6100 through metal-mediated carbenoid C–H bond insertion reactions.



Scheme 1. Selective functionalization of primary (1°) over secondary (2°) C–H bonds of alkanes in the metal-mediated C–C bond-formation reactions reported in this work.

Our studies in this work were inspired by previous work from the research groups of Callot[6a,b] and Suslick.[7] In the 1980s, Callot and co-workers reported that the primary C–H bond selectivity for the reaction of linear alkanes with ethyl diazoacetate (N_2CHCO_2Et, EDA) catalyzed by [Rh(por)I] ($H_2(por)$ = meso-tetraarylporphyrin) increases with the size of the *ortho* groups H, Me, or Cl of the meso-aryl rings. We envisioned that replacing these *ortho* groups with bulkier phenyl groups, coupled with changing the α hydrogen atom of EDA to a phenyl group, would enhance the selectivity for primary C–H bonds. Therefore, our attention was directed to developing an intermolecular C–H bond insertion reaction of alkanes with $N_2C(Ph)CO_2R$[4b,c] catalyzed by the rhodium complex of meso-tetrakis(2,4,6-triphenylphenyl)porphyrin

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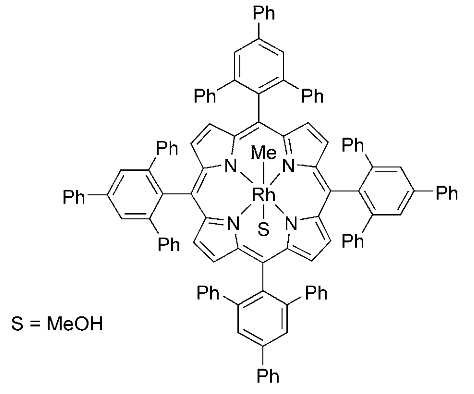
[H_2(ttppp)]. The H_2(ttppp) ligand, a bis-pocket porphyrin first synthesized in 1983 by Suslick and Fox,[7a] was previously shown to dramatically enhance the selectivity in the hydroxylation of alkanes, with a primary/secondary selectivity of up to approximately 0.82:1 obtained for [Mn(ttppp)(OAc)].[7b]

To insert rhodium into H_2(ttppp), we employed a method analogous to that for the preparation of [Rh(ttp)(Me)][8a] and [Rh(tmp)(Me)].[8b] Reaction of [$Rh(CO)_2Cl]_2$ with H_2(ttppp) in toluene, followed by treatment with $NaBH_4$, MeI, and MeOH, afforded [Rh(ttppp)(Me)(MeOH)] (**I**). Complex **I** was characterized by ^{1}H NMR and UV/Vis spectroscopy as well as mass spectrometry. Its structure has been determined by X-ray crystallography[9] and is shown in Figure 1 (see also Table S1 in the Supporting Information). This complex has Rh–C(Me) and Rh–O(MeOH) distances of 2.028(15) Å and 2.507(16) Å, respectively; the former is similar to that of 2.027(4) Å in [Rh(F_{28}-tpp)(Me)] (H_2(F_{28}-tpp) = 2,3,7,8,12,13,17,18-octafluoro-meso-tetrakis(pentafluorophenyl)porphyrin).[10]



[Rh(ttppp)(Me)(MeOH)] **I**

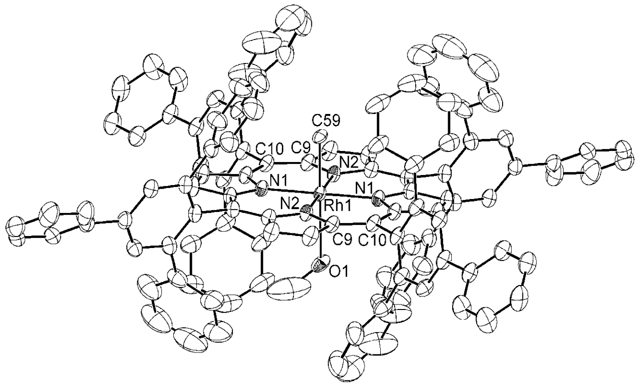
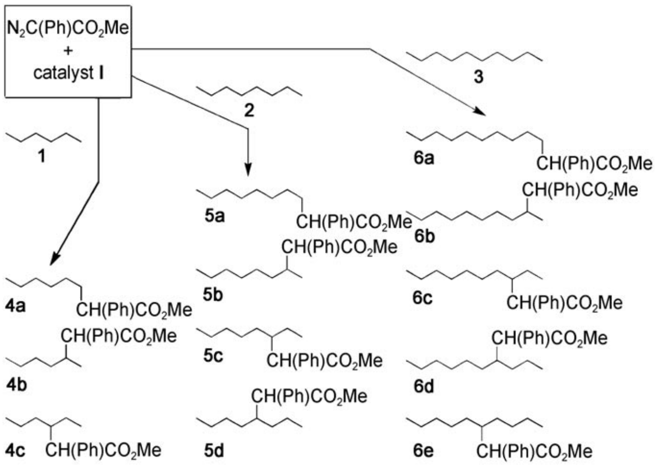
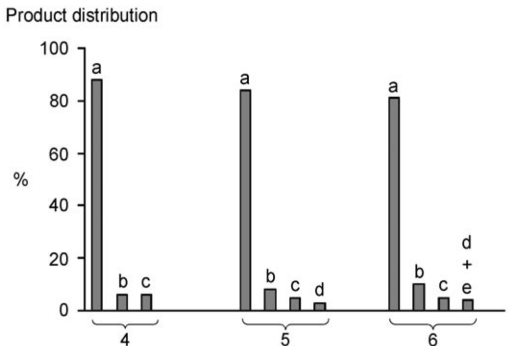


Figure 1. X-ray crystal structure of **I** with omission of hydrogen atoms. Thermal ellipsoid probability: 30%.

Access to the rhodium atom in **I** is difficult because of steric hindrance (Figure 1 and Figure S1 in the Supporting Information). We investigated whether this rhodium bis-pocket porphyrin complex could react with the sterically encumbered $N_2C(Ph)CO_2R$ to form the corresponding metal–carbene intermediates for subsequent reactions with alkanes, in a similar fashion to metal catalysts for carbenoid transfer reactions.[4a,b] We found that **I** is an active catalyst for the reaction of $N_2C(Ph)CO_2Me$ with *n*-hexane (**1**), *n*-octane (**2**), and *n*-decane (**3**). These reactions afforded the C–H bond insertion products **4–6** with remarkably high selectivity for the primary C–H bonds (Scheme 2).



Product	Yield [%]	1°/2°
4a + **4b** + **4c**	51	9.8:1
5a + **5b** + **5c** + **5d**	55	10.5:1
6a + **6b** + **6c** + **6d** + **6e**	58	11.4:1

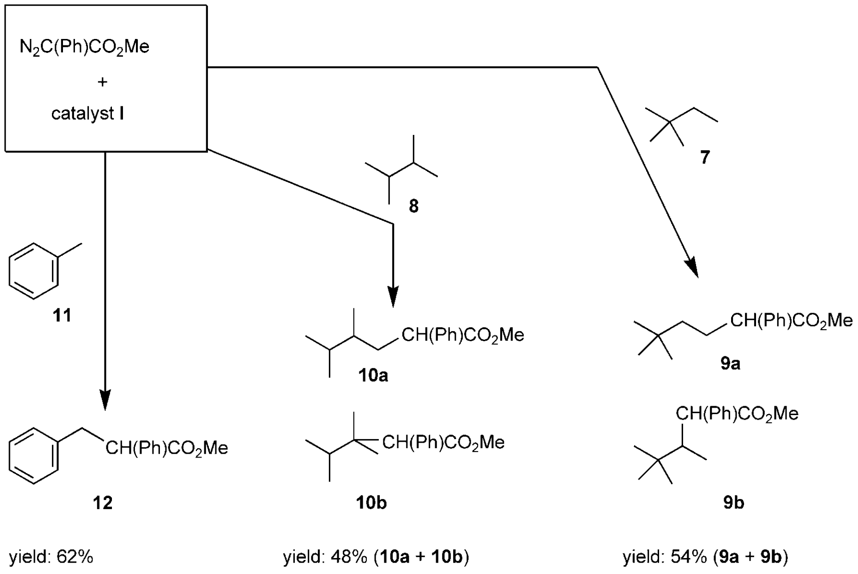


Scheme 2. Intermolecular C–H bond insertion of *n*-alkanes **1–3** with $N_2C(Ph)CO_2Me$ catalyzed by **I**. Reaction conditions: $N_2C(Ph)CO_2Me$ (0.1 mmol), alkane (4 mL), **I** (2.5 mol%), 80°C under N_2, 24 h. Conversion of $N_2C(Ph)CO_2Me$: 100%. The yields (based on $N_2C(Ph)CO_2Me$) are for isolated products. The primary/secondary ratio was normalized for the relative number of hydrogen atoms.

Addition of $N_2C(Ph)CO_2Me$ (0.1 mmol) in *n*-hexane (2 mL) to a mixture of **I** (2.5 mol%) and *n*-hexane (2 mL) at 80°C over 20 h, followed by stirring the mixture at 80°C for 4 h, gave **4a–c** in an overall yield of 51% (based on $N_2C(Ph)CO_2Me$), with a primary/secondary selectivity of 9.8:1. Changing the catalyst to [Rh(ttp)(Me)] or [Rh(tmp)(Me)] (both 1.5 mol%; H_2(ttp) = meso-tetrakis(*p*-tolyl)porphyrin, H_2(tmp) = meso-tetramesitylporphyin) which contain a sterically less demanding porphyrin ligand lowered the primary/secondary selectivity of **4a–c** to 0.9:1 or 3.4:1, respectively (Scheme S2 in the Supporting Information). For substrates *n*-octane and *n*-decane, the primary/secondary selectivities of catalyst **I** reached 10.5:1 (**5a–d**) and 11.4:1 (**6a–e**).

When EDA was used instead of $N_2C(Ph)CO_2Me$, the **I**-catalyzed C–H bond insertion products for substrates **1** and **3** were obtained in up to 63 % yield (reaction time: 24 h), with a primary/secondary selectivity of (2.7–3.2):1 (Table S2 in the Supporting Information).

Branched alkanes 2,2-methylbutane (**7**) and 2,3-methylbutane (**8**) also underwent C–H bond insertion with $N_2C(Ph)CO_2Me$ in the presence of catalyst **I**, affording **9a**,**b** or **10a**,**b** in 48–54 % yields (Scheme 3). The primary/secondary selectivity for **7** is 6.7:1. Notably, although **7** contains two types of primary C–H bonds—one bonded to the secondary carbon atom and the other bonded to the quaternary carbon atom, only the former underwent C–H bond insertion with $N_2C(Ph)CO_2Me$. This demonstrates an excellent regioselectivity in the I-catalyzed primary C–H bond insertion.



Scheme 3. Intermolecular C–H bond insertion of **7**, **8**, and **11** with $N_2C(Ph)CO_2Me$ catalyzed by **I**. The reaction conditions are the same as those indicated in the legend of Scheme 2. Conversion of $N_2C(Ph)CO_2Me$: 100%. The primary/secondary or primary/tertiary ratio was normalized for the relative number of hydrogen atoms.

$N_2C(Ph)CO_2Me$ was reacted with toluene (**11**) in the presence of **I** for 24 h to give the primary C–H bond insertion product **12** in 62 % yield (Scheme 3). No cyclopropanation product was observed in the ^1H NMR spectrum of the reaction mixture. In contrast, the previously reported reaction of toluene with $N_2C(p\text{-}BrC_6H_5)CO_2Me$ catalyzed by $[Rh_2((S)\text{-}dosp)_4]$ ((*S*)-dosp = *N*-[(4-dodecylphenyl)sulfonyl]-(*S*)-prolinate) mainly gave cyclopropanation products with the primary C–H bond insertion product formed in 14 % yield.[11]

The high selectivity in the **I**-catalyzed C–H bond insertion reactions can be rationalized by the steric interaction between the substrates and the putative rhodium–carbene complexes of the bis-pocket porphyrin. Previously, Kodadek and coworkers provided strong evidence for a rhodium–porphyrin–carbene complex intermediate in the cyclopropanation of alkenes with EDA catalyzed by rhodium porphyrins,[12] although such a metal–carbene species has not been observed. We propose that the reaction of EDA or $N_2C(Ph)CO_2Me$ with **I** generates the carbene complexes $[Rh(ttppp)(CHCO_2Et)(X)]$ or $[Rh(ttppp)(C(Ph)CO_2Me)(X)]$ (X could be, for example, Me or solvent) in a fashion analogous to the reactions catalyzed by other rhodium complexes.[13] We have performed density functional theory (DFT) calculations on the hypothetical compounds $[Rh(ttppp)(C(Ph)CO_2Me)(Cl)]$ and $[Rh(por^0)(C(Ph)CO_2Me)(Cl)]$ (where por^0 is the unsubstituted porphyrin ring), which showed that these complexes are, at least in theory, stable species (see the Supporting Information). Figure 2 shows the optimized structure of $[Rh(ttppp)(C(Ph)CO_2Me)(Cl)]$; the calculated Rh–C distance of 1.982 Å is slightly longer than that in the optimized structure of $[Rh(por^0)(C(Ph)CO_2Me)(Cl)]$ (1.969 Å, Figure S3 in the Supporting Information). Based on the optimized structure in Figure 2, it is evident that the axial phenyl groups of ttppp would impose a significantly larger steric hindrance for secondary than for primary C–H bonds that attack the carbene group in a concerted manner,[13] which accounts for the high primary/secondary selectivity shown in Scheme 2 and Scheme 3.

The reaction of $[Rh(oep)(Me)]$ (H_2-(oep) = 2,3,7,8,12,13,17,18-octaethylporphyrin) with EDA in the presence of acetic acid has been shown to give an N-substituted rhodium–porphyrin complex $[Rh(N\text{-}CH_2CO_2Et\text{-}oep)(Me)]ClO_4$.[14] In this work, we isolated and structurally characterized $[Rh(N\text{-}CH_2CO_2Et\text{-}ttp)(Me)]ClO_4$ from the reaction of $[Rh(ttp)(Me)]$ with EDA (Figure 3 and Figure S2 in the Supporting Information).[9] However, treatment of this complex with *n*-hexane or cyclohexane (**13**) at reflux afforded no C–H bond insertion product; this observation suggests that the N-

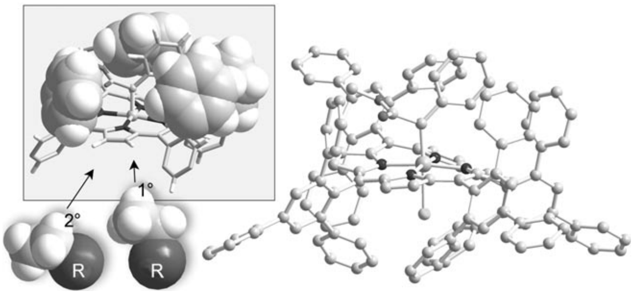


Figure 2. Optimized structure (B3LYP) of $[Rh(ttppp)(C(Ph)CO_2Me)(Cl)]$. The inset shows a part of the structure with axial phenyl groups of ttppp in spacefill representation. A spacefill representation of alkanes with either primary and secondary C–H bonds approaching the carbene group is shown in the lower left corner.

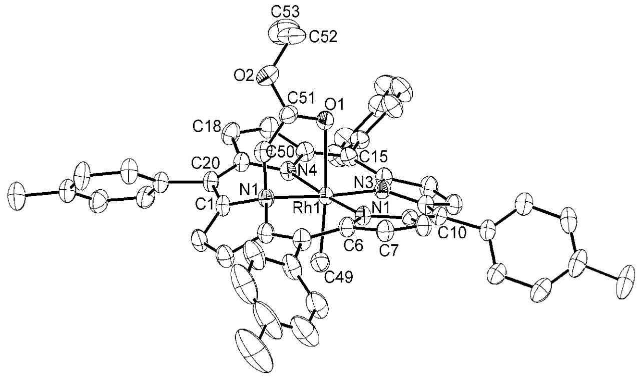
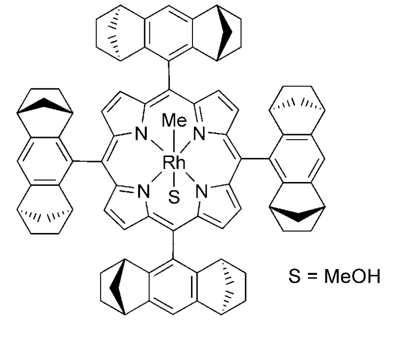


Figure 3. X-ray crystal structure of [Rh(N-CH_2CO_2Et-ttp)(Me)]ClO_4 with omission of the counterion. Thermal ellipsoid probability: 30%.

substituted rhodium–porphyrin complex is not the catalytically active intermediate. Similarly, rhodium–corrole analogues have been shown not to be true intermediates in the related catalytic cyclopropanation reaction of styrenes.[15]

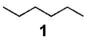
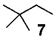
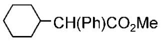
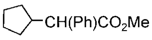
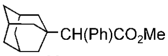
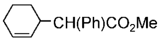
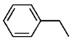
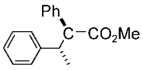
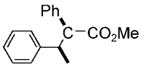
Davies et al. demonstrated that [Rh_2((*S*)-dosp)$_4$] exhibits high enantio- and chemoselectivity in catalyzing intermolecular C–H bond insertion reactions of alkanes with aryl diazoacetates $N_2C(Ar)CO_2R$.[4b] These [Rh_2((*S*)-dosp)$_4$]-catalyzed reactions exclusively occur at secondary or tertiary C–H bonds, leaving the primary C–H bonds unfunctionalized.[16] Therefore, the quest for an enantioselective carbenoid transfer reaction that is highly selective for primary C–H bonds of alkanes remains a challenge.

In view of the high primary/secondary selectivity obtained with catalyst **I**, we examined the enantioselective intermolecular C–H bond insertion with $N_2C(Ph)CO_2Me$ catalyzed by [Rh(D_4-por*)(Me)(MeOH)] (**II**, H_2(D_4-por*) = meso-tetrakis-{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethano-anthracen-9-yl}porphyrin), which contains a sterically encumbered chiral porphyrin ligand first synthesized by Halterman and Tan.[17] The preparation of **II** is similar to that of **I**. Reaction of $N_2C(Ph)CO_2Me$ with *n*-hexane, 2,2-dimethylbutane, cyclohexane, cyclopentane (**14**), adamantane (**15**), cyclohexene (**16**), or ethylbenzene (**17**) in the presence of **II** (0.1–1.5 mol%) at 60°C afforded C–H bond insertion products **4**, **9**, and **18**–**22** in up to 80% yield and up to 93% *ee* (Table 1). The best enantiocontrol (92 and 93% *ee*) was achieved for cyclohexane and cyclopentane (Table 1, entries 3 and 4).



[Rh(D_4-por*)(Me)(MeOH)] **II**

Table 1: Enantioselective intermolecular C–H bond insertion catalyzed by **II**.[a]

Entry	Substrate	Product	Yield[b] [%]	*ee*[c,d] [%]	Primary/ secondary[e]
1	 **1**	**4a** + **4b** + **4c**	66	68 (**4a**)	3.5:1
2	 **7**	**9a** + **9b**	55	65 (**9a**)	3.8:1
3	 **13**	 **18**	80	92	
4	 **14**	 **19**	64	93	
5	 **15**	 **20**	78	88	
6	 **16**	 **21**	43[f]	71[g]	
7	 **17**	 **22a**	45	85	
		 **22b**	16	77	

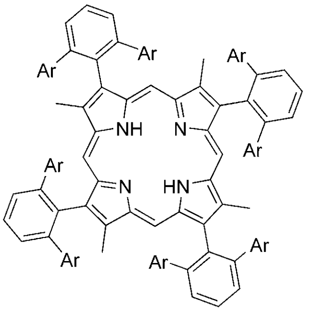
[a] Reaction conditions: $N_2C(Ph)CO_2Me$ (0.1 mmol); **1**, **7**, **13**, or **14** (4 mL); **15** (2 equiv), **16** or **17** (5 equiv) in 1,2-dichloroethane (4 mL); **II** (0.1 mol% for **13**–**17**, 1.5 mol% for **1** and **7**); 60°C under N_2; 4 h (**13**–**15**) or 24 h (others). Conversion of $N_2C(Ph)CO_2Me$: 100%. [b] Determined by GC–MS after chromatography (based on $N_2C(Ph)CO_2Me$). [c] Determined by HPLC with chiral-OD column. [d] Absolute configuration not determined. [e] Normalized for the relative number of hydrogen atoms. [f] The ratio of two diastereomers is 60:40. The reaction was performed in the presence of 4 Å molecular sieves. The cyclopropanation product was also formed in 14% yield. [g] Determined after catalytic hydrogenation of **21** (H_2/Pd on C).

Two features of the enantioselective C–H bond insertion reactions catalyzed by **II** were noted: 1) For 2,2-dimethylbutane, an unreactive substrate for catalyst [Rh_2((*S*)-dosp)$_4$],[16b] the C–H bond insertion products **9a**,**b** were obtained in 55% yield by employing **II** as catalyst (Table 1, entry 2) and 2) in contrast to the selective secondary or tertiary C–H bond functionalization catalyzed by [Rh_2((*S*)-dosp)$_4$],[16] the **II**-catalyzed reactions of *n*-hexane and 2,2-dimethylbutane with $N_2C(Ph)CO_2Me$ preferentially afforded primary C–H bond insertion products **4a** and **9a**, respectively, albeit with moderate enantioselectivity (65–68% *ee*). For both substrates, the selectivity for primary C–H bonds is about four times that for secondary bonds (Table 1, entries 1 and 2). To the best of our knowledge, these are the first metal-catalyzed enantioselective carbenoid insertion reactions that feature significantly higher selectivity for primary than for secondary C–H bonds.

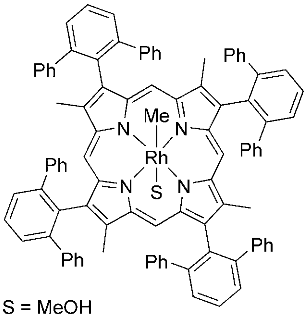
Catalysts **I** and **II** are recyclable and robust. For the reaction of *n*-decane with EDA using catalyst **I** (0.1 mol%) and the reaction of cyclohexane with $N_2C(Ph)CO_2Me$ using catalyst **II** (0.1 mol %), the catalysts could be reused at least five times without significantly lowering the primary/secondary selectivity or enantioselectivity (see Table S3 in the Supporting Information), and the total number of product turnovers reached 6477 after recycling the catalyst five times. When 0.01 mol % of **II** was used, the reaction between cyclohexane and $N_2C(Ph)CO_2Me$ at 60 °C for 8 h gave **18** in 61 % yield and 90 % *ee*, corresponding to a product turnover number of 6100.

Reactions were also carried out on the gram scale. Treatment of $N_2C(Ph)CO_2Me$ (3 g) and **I** (2 mol %) with toluene (150 mL) at 80 °C for 25 h afforded **12** (2.26 g, 56 % yield), together with the dimers (43 % yield) arising from coupling of $N_2C(Ph)CO_2Me$. The reaction of $N_2C(Ph)CO_2Me$ (3 g) and **II** (0.1 mol %) with cyclohexane (150 mL) at 60 °C for 10 h gave **18** (2.88 g, 73 % yield) in 91 % *ee*.

To circumvent the difficulty of the bis-pocket porphyrin synthesis, we directed our attention to porphyrin ligands **23** and prepared 1,3,5,7-tetramethyl-2,4,6,8-tetraterphenylporphyrin (H_2ttmp), reported by Chang and co-workers,[18] in 35 % yield. Its rhodium complex, [Rh(tmttp)(Me)(MeOH)] (**III**), was subsequently prepared, the X-ray crystal structure of which is shown in Figure S4 in the Supporting Information.[9] The reactions of $N_2C(Ph)CO_2Me$ (0.1 mmol) with *n*-hexane, *n*-octane, and *n*-decane (4 mL) catalyzed by **III** (2.5 mol %) at 80 °C for 24 h gave **4–6** in 50–55 % yields, with a primary/secondary selectivity of 6.5:1 (**4a–c**), 6.7:1 (**5a–d**), and 7.2:1 (**6a–e**). Further studies are underway to enhance the primary/secondary selectivity by tuning the Ar groups in **23**.



23



S = MeOH
[Rh(tmttp)(Me)(MeOH)] **III**

In conclusion, by employing $N_2C(Ph)CO_2Me$ and robust sterically encumbered rhodium–porphyrin catalysts, we have demonstrated highly selective primary C–H bond functionalization and enantioselective secondary C–H bond functionalization in C–C bond formations by metal-catalyzed carbenoid transfer reactions.

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