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Trapping Reactive Metal–Carbene Complexes by a Bis-Pocket Porphyrin: X-ray Crystal Structures of Ru=$CHCO_2Et$ and *trans*-[Ru(CHR)(CO)] Species and Highly Selective Carbenoid Transfer Reactions

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The formation of C−C bonds by a metal-catalyzed reaction of diazo compounds $N_2CR^1R^2$ with hydrocarbons, via putative metal–carbene intermediates, has a wide spectrum of applications in organic synthesis.[1] Identification of the reactive metal–carbene intermediates in these catalytic processes is of great importance for elucidating the reaction mechanisms. Since the isolation of [Os($CHCO_2Et$)(ttp)] (ttp = 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato(2−)) by Woo and co-workers[2] and [Ru($CHCO_2R$)Cl_2(pybox)] (R = aryl groups; pybox = 2,6-bis[(4′*S*)-isopropyloxazolin-2′-yl]pyridine) by Nishiyama and co-workers[3] from the reaction of diazo compounds with metal catalysts, a number of reactive metal–carbene complexes have been isolated or directly observed from such reactions.[2–4] Characterization of these reactive complexes by X-ray crystal analysis has been realized for the M=CR^1R^2 ($R^1 \neq H$ and $R^2 \neq H$) species.[4a,b,c,h–j] Recently, Simonneaux and co-workers structurally characterized [Ru{$CHCO_2$(2,6-$t$$Bu_2$-4-Me-$C_6H_2$)}(thf)(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinato(2−)),[5] an M=$CHCO_2R$ complex kinetically stabilized by a bulky R group.

While N_2CHCO_2Et (EDA) has been used in numerous studies on metal-catalyzed carbenoid transfer reactions, particularly intermolecular cyclopropanation of alkenes,[1] the corresponding reactive M=$CHCO_2Et$ intermediates have sparsely been isolated,[2,4c,d] in contrast to the report of a good number of reactive M=CR^1R^2 ($R^1 \neq H$ and $R^2 \neq H$) complexes.[6] To the best of our knowledge, only one M=$CHCO_2Et$ complex has been structurally characterized in the literature, that is, Werner and co-workers′ carbene complex [Os($CHCO_2Et$)(Cl)(CO)(H)($P$$i$$Pr_3$)$_2$],[7] which has not been reported to undergo carbenoid transfer with hydrocarbons. Given the effective shielding of the carbene center by bulky 2,6-$t$$Bu_2$-4-Me-$C_6H_2$ in the structure of [Ru{$CHCO_2$(2,6-$t$$Bu_2$-4-Me-$C_6H_2$)}(thf)(tpp)],[5] the X-ray crystal structure characterization of reactive M=$CHCO_2Et$ species, in which the Et group is too small to shield the carbene center, remains a challenge.

A strategy for kinetically stabilizing reactive M=$CHCO_2Et$ complexes is to protect the carbene center with sterically encumbered auxiliary ligands. In this regard, we turned our attention to the bis-pocket porphyrin ligand 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinato(2−) (ttppp), which was first synthesized by Suslick and co-workers.[8] Metalloporphyrin-catalyzed alkene cyclopropanation with diazo compounds, including EDA, has received a considerable attention[9] since the pioneering work by Callot and Piechocki.[10] By using simple porphyrin ligand ttp and sterically encumbered porphyrin ligands 5,10,15,20-tetramesitylporphyrinato(2−) (tmp) and Halterman's porphyrin 5,10,15,20-tetrakis{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl}porphyrinato(2−) (D_4-por*),[11] Collman and co-workers isolated [Ru($CHCO_2Et$)(por)] (por = ttp, tmp),[12] Woo and co-workers isolated [Os($CHCO_2Et$)(ttp)],[2] and we observed the formation of [Ru($CHCO_2Et$)(D_4-por*)] in solution.[13] But characterization of these M=$CHCO_2Et$ porphyrin complexes by X-ray crystal analysis has not been realized. On the other hand, a wide variety of [M(CR^1R^2)(por)] and [M(CR^1R^2)(L)(por)] (M = Ru, Os; $R^1 \neq H$, $R^2 \neq H$; L = σ donor, such as pyridine or 1-methylimidazole) have been generated or isolated from

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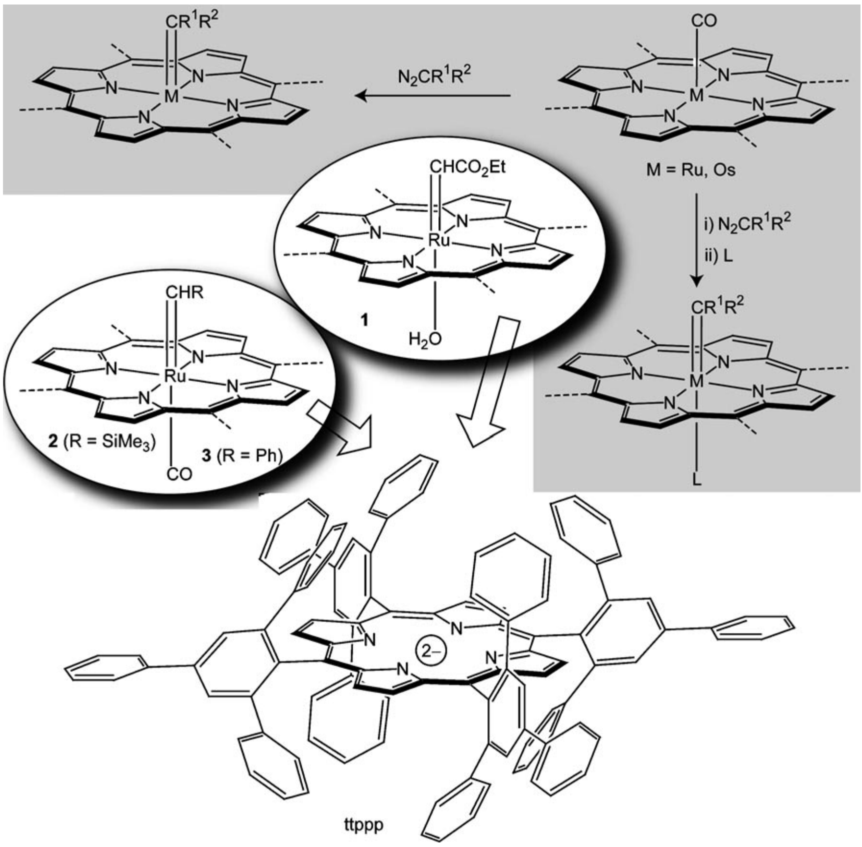
treatment of [M(CO)(por)] with $N_2CR^1R^2$ (Scheme 1, shaded area),[4b,e,9b,14] consistent with the proposed involvement of $M{=}CR^1R^2$ intermediates in alkene cyclopropanation with $N_2CR^1R^2$ catalyzed by [M(CO)(por)] (M = Ru, Os).[2,4e,f,9b,c,14a,15] Recently, we reported a highly selective carbenoid insertion into primary C−H bonds of alkanes catalyzed by [Rh(Me)(MeOH)(ttppp)].[16] A putative [Rh($CHCO_2Et$)(ttppp)] intermediate was proposed based on the result of DFT calculations.



Scheme 1. Formation of $M{=}CR^1R^2$ complexes from treatment of [M(CO)(por)] with $N_2CR^1R^2$ and schematic structures of **1**–**3**.

Herein, we report the isolation and X-ray crystal structure of [Ru($CHCO_2Et$)(H_2O)(ttppp)] (**1**, Scheme 1) and its reactivity toward alkene cyclopropanation, and also the following findings originating from the sterically encumbered ttppp ligand: 1) A dramatic change in the chemoselectivity of [Ru(CO)(por)]-catalyzed reactions of EDA, 2) isolation and X-ray crystal structure determination of [Ru(CHR)(CO)(ttppp)] (**2**: R = $SiMe_3$, **3**: R = Ph; Scheme 1). There are no precedents in the literature for the crystal structures of carbene complexes of metalloporphyrins with a *trans* CO ligand; their formation provides useful information on the mechanisms of the carbenoid transfer reactions catalyzed by carbonyl metalloporphyrins.

The insertion of ruthenium into ttppp was accomplished by treating [$Ru_3(CO)_{12}$] with H_2(ttppp) in 1,2,4-trichlorobenzene at 190 °C to give [Ru(CO)(ttppp)] in 85 % yield. A slow diffusion of hexane into a solution of [Ru(CO)(ttppp)] and THF in CH_2Cl_2 gave crystals of [Ru(CO)(thf)(ttppp)]. Treatment of [Ru(CO)(ttppp)] with excess N_2CHR (R = CO_2Et, $SiMe_3$, Ph) in CH_2Cl_2 at room temperature for 20 min, followed by layering hexane or isopropanol on the top of the reaction mixtures, gave diffraction-quality crystals of **1**–**3**. The crystal data[17] and the X-ray crystal structures of [Ru(CO)(thf)(ttppp)] and **3** are included in the Supporting Information (Tables S1 and S2, Figures S1 and S2). The Ru−C(CO) length of [Ru(CO)(thf)(ttppp)] is 1.825(5) Å, which is comparable to those of other carbonyl ruthenium porphyrin complexes (1.77(2)–1.838(9) Å).[18] The X-ray crystal structures of **1** and **2** are depicted in Figure 1.

Complex **1** shows a Ru=C length of 1.847(13) Å and a Ru=C−C angle of 137.6(10)°. The former falls in the Ru=C length range of 1.806(3)–1.876(3) Å, whereas the latter is considerably larger than the Ru=C−C angle of ≈125° found for the $Ru{=}CR^1R^2$ ($R^1 \neq H$, $R^2 \neq H$) porphyrin complexes.[14b] A water molecule *trans* to the $CHCO_2Et$ carbene ligand is weakly bound to ruthenium in **1**, with a Ru···O(H_2O) length of 2.753(13) Å.

In contrast, the Ru=C length of 2.027(4) Å found in **2** is much longer than that found in **1**, although the latter has a Ru=C−Si angle of 140.0(3)° similar to the Ru=C−C angle in the former. The Ru−C(CO) bond of **2** is also substantially lengthened to 2.125(7) Å, about 0.3 Å longer than that in [Ru(CO)(thf)(ttppp)]. This indicates that both the CO and $CHSiMe_3$ ligands have a large *trans* effect.

Complex **3** is disordered between two spatial orientations (one is depicted in Figure S2 in the Supporting Information) because the Ru atom lies on the inversion center of the space group *C2/c*. In the structure refinement, the best *R* value was obtained for a structure in which the Ru-bound C atoms of CHPh and CO occupy the same position, with a Ru−C length of 1.953(1) Å (see the Supporting Information). The CO ligand in **3** can be readily replaced by a coordinating solvent, such as H_2O, MeOH, or THF.

To the best of our knowledge, structurally characterized metal complexes that contain a CHR carbene ligand *trans* to a CO ligand have not been reported previously. Two re-

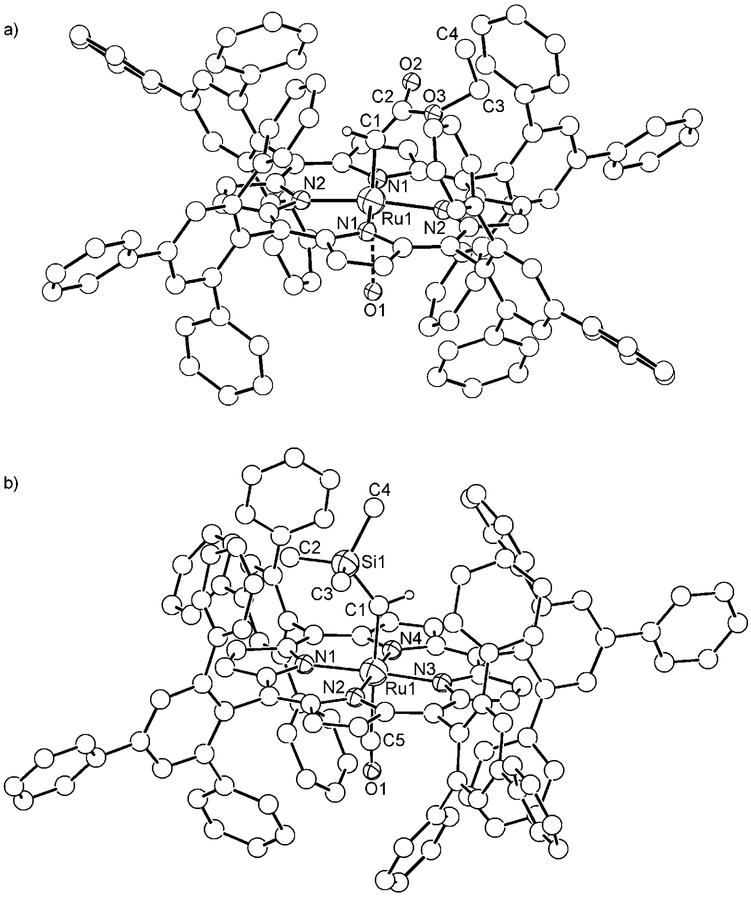


Figure 1. Structures of a) **1** and b) **2**. Hydrogen atoms have been omitted for clarity, with the exception of those bonded to the carbene carbon atoms.

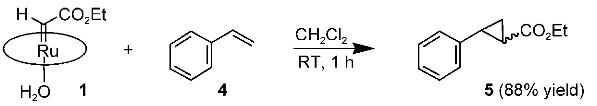
lated examples are the N-heterocyclic carbene (NHC) complexes $[Ru(NHC)(CO)(NH_3)_4][PF_6]_2$ (Ru−C(NHC) 2.128(4) Å, Ru−C(CO) 1.849 Å)[19a] and [Ru(NHC)(CO)(Cl)(H)$(PPh_3)_2$] (Ru−C(NHC) 2.1282(18) Å, Ru−C(CO) 1.884(2) Å),[19b] both of which have rather short M−C(CO) lengths compared with **2**. A nonporphyrin diphenylcarbene complex [Ru(CPh_2)(CO)(tmtaa)] (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldibenzo-[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecinato(2−)) was reported,[20] but its structure has not been determined by X-ray crystal analysis.

The structure determination of **2** provides a measure of the *trans* influence of a non-NHC carbene ligand on the M−CO bonding, and vice versa. For this purpose, a more complicated case is the crystal structure of [W(CPh_2)$(CO)_5$].[21] This tungsten complex not only has a long W−C(CPh_2) length of 2.14(2) Å and a W−C(CO *trans* to CPh_2) length of 2.04(2) Å, but also contains four CO ligands *cis* to the CPh_2 ligand with W−C(CO) lengths of 1.98(2), 2.02(2), 2.02(2), and 2.03(3) Å.

IR measurements revealed that the crystals of **2** and **3** readily lose their CO ligands during sample preparation. To observe the ν(CO) bands in these complexes, we monitored the treatment of [Ru(CO)(ttppp)] with N_2CHR (R = $SiMe_3$, Ph; 2 equiv) in CH_2Cl_2 at room temperature by using in situ IR spectroscopy. As the reactions proceeded, a new band at $\tilde{\nu} = 2016\ cm^{-1}$ that is markedly different from the ν(CO) band of [Ru(CO)(ttppp)] ($\tilde{\nu} = 1952\ cm^{-1}$) appeared in the IR spectra of the reaction mixtures. We tentatively attribute this new band to the weakly bound CO *trans* to the CHR ligand. Interestingly, the reaction of [Ru(CO)(ttppp)] with EDA (3 equiv) also generated a similar new band at $\tilde{\nu} = 2016\ cm^{-1}$, which eventually vanished within 1 h, accompanied by formation of diethyl maleate. This reveals the possible formation of [Ru($CHCO_2Et$)(CO)(ttppp)] in the reaction.

The ^1H NMR spectrum of **1** in $CDCl_3$ shows a Ru=CH signal at $\delta = 13.07$ ppm, similar to those of [Ru($CHCO_2Et$)(ttp)] ($\delta = 13.43$ ppm)[12a] and [Ru($CHCO_2Et$)(tmp)] ($\delta = 13.79$ ppm).[12b] For complex **2**, the ^1H NMR spectrum in $CDCl_3$ shows a Ru=CH signal at $\delta = 18.55$ ppm, which is comparable to that of [Ru($CHSiMe_3$)(ttp)] ($\delta = 19.44$ ppm).[22] The Ru=CH signal of **3** is located at $\delta = 12.38$ ppm. Lowering the temperature from 27 to −60 °C did not result in either significant broadening or splitting of the ^1H NMR signals for **2** and **3**. In the ^{13}C NMR spectrum of **3**, signals at $\delta = 298.19$ and 199.51 ppm were discernible and could be assigned to Ru=C and Ru−CO, respectively. Upon prolonged standing at room temperature, the solution of **2** in $CDCl_3$ showed no Ru=CH proton resonance, and [Ru(CO)(ttppp)] was isolated in 54 % yield from the solution.

Complex **1** is reactive toward the stoichiometric cyclopropanation of styrene (**4**). Treatment of **1** with **4** (10 equiv) in CH_2Cl_2 at room temperature gave **5** in 88 % yield with a *trans*/*cis* ratio of 20:1 (Scheme 2). Both the yield and *trans*/*cis* ratio are similar to those obtained for the same product in the cyclopropanation of styrene (2 mmol) with EDA (0.20 mmol) catalyzed by 1 mol % [Ru(CO)(ttppp)] in

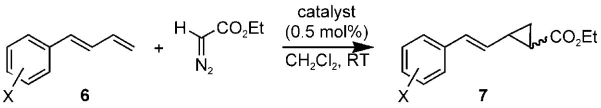


Scheme 2. Stoichiometric cyclopropanation of styrene (**4**) by **1**.

CH_2Cl_2 for 4 h (85 % yield, *trans*/*cis* 19:1). These results, along with the facile formation of **1** by treating [Ru(CO)(ttppp)] with EDA, suggest that [Ru($CHCO_2Et$)(L)(ttppp)] is an intermediate in the [Ru(CO)(ttppp)]-catalyzed styrene cyclopropanation with EDA. At this point, we do not exactly know the ligand *trans* to Ru=$CHCO_2Et$ in [Ru($CHCO_2Et$)(L)(ttppp)]. As 64 % of [Ru(CO)(ttppp)] was recovered from the carbenoid transfer reaction between styrene and EDA catalyzed by [Ru(CO)(ttppp)], it is likely that [Ru($CHCO_2Et$)(CO)(ttppp)] is a possible reactive intermediate.

To reveal the impact of ttppp on the diastereoselectivity in [Ru(CO)(por)]-catalyzed cyclopropanation of alkenes, we compared the catalytic properties of [Ru(CO)(ttppp)] and [Ru(CO)(tmp)] for the reactions of aryl-conjugated dienes (**6a–f**) with EDA (see Table 1). Both catalysts resulted in the formation of cyclopropanation products **7a–f** in excellent yields (≈95 %, total yield of *trans*- and *cis*-**7**) with *trans* selectivity. The *trans*/*cis* ratios obtained by using catalyst [Ru(CO)(ttppp)] are (6.2–9.0):1, substantially higher than those of (1.2–2.0):1 obtained using catalyst [Ru(CO)(tmp)]. Note that previous reports on the metal-catalyzed cyclopropanation of **6** with EDA to form **7** are rare. Doyle and co-workers reported a *trans*/*cis* ratio of 1.6:1 for **7a** in the [$Rh_2(OAc)_4$]-catalyzed cyclopropanation of **6a** with EDA.[23a] In a recent report by Katsuki and co-workers,[23b] the Ir^{III}–salen-catalyzed cyclopropanation of **6a** with EDA gave **7a** in 99 % yield with a *cis*-selectivity (*cis*/*trans* up to ≈3.8:1).

Table 1. Comparison of the catalytic properties of [Ru(CO)(ttppp)] and [Ru(CO)(tmp)] in the cyclopropanation of **6** with EDA.[a]

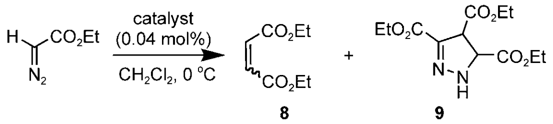


Entry	X	[Ru(CO)(ttppp)] Yield of **7**[b] [%]	[Ru(CO)(ttppp)] *trans*/*cis*[c]	[Ru(CO)(tmp)] Yield of **7**[b] [%]	[Ru(CO)(tmp)] *trans*/*cis*[c]
1	H (**6a**)	97 (**7a**)	7.1:1	96 (**7a**)	1.9:1
2	*p*-OMe (**6b**)	96 (**7b**)	7.0:1	96 (**7b**)	1.7:1
3	*p*-Br (**6c**)	93 (**7c**)	7.7:1	94 (**7c**)	1.8:1
4	*p*-NO_2 (**6d**)	94 (**7d**)	6.2:1	94 (**7d**)	1.2:1
5	*m*-NO_2 (**6e**)	94 (**7e**)	7.1:1	95 (**7e**)	1.3:1
6	*p*-OBn (**6f**)	95 (**7f**)	9.0:1	95 (**7f**)	2.0:1

[a] Reaction conditions: **6** (0.2 mmol), EDA (0.24 mmol), catalyst (0.001 mmol), CH_2Cl_2 (3 mL), RT. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy.

A significant change in chemoselectivity was found for the [Ru(CO)(por)]-catalyzed decomposition of EDA upon changing the porphyrin ligand from tmp to ttppp (Table 2). At a catalyst loading of 0.04 mol %, the decomposition of EDA catalyzed by [Ru(CO)(tmp)] at 0 °C for 4 h gave **8** in 93 % yield (*cis*/*trans* 55:1). However, under the same conditions, a much slower decomposition of EDA was observed when using [Ru(CO)(ttppp)], giving **8** in only 11 % yield after 42 h. The major product is **9**, which was isolated in 79 % yield.

Table 2. Decomposition of EDA catalyzed by [Ru(CO)(por)] (por = ttppp, tmp).



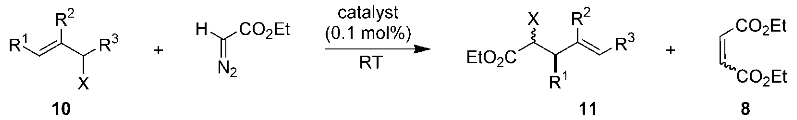
Catalyst	*t* [h]	Yield[a] [%]	**8**:**9**[b]
[Ru(CO)(tmp)]	4	93 (**8**)[c]	–
[Ru(CO)(ttppp)]	42	11 (*cis*-**8**)[d] 79 (**9**)	4.2:1

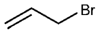
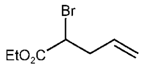
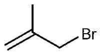
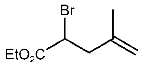
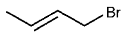
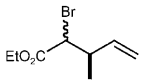
[a] Isolated yield. [b] Determined by ^{1}H NMR spectroscopy. [c] Ratio of *cis*-**8**/*trans*-**8** = 55:1; no **9** was detected. [d] No *trans*-**8** was detected.

Also, there is an enormous difference in reactivity between [Ru(CO)(ttppp)] and [Ru(CO)(tmp)] in catalyzing the reaction of allyl bromides **10a–c** with EDA to afford **11a–c** (Table 3). Such reactions of allyl halides with EDA catalyzed by metal complexes are sparse.[24] A proposed mechanism involves attack of metal–carbene intermediates by allyl halides to generate halonium ylides; the latter undergo [2,3]-sigmatropic rearrangement to give the observed products.[24] With catalyst [Ru(CO)(tmp)] (0.1 mol %), the reaction of **10a–c** with EDA gave **8** as the major product, with a low **11**:**8** yield ratio of (0.15–0.43):1. A lower **11**:**8** yield ratio of 0.075:1 was previously reported for the [Ru(CO)(tpp)]-catalyzed reaction of **10a** with EDA.[24c] Remarkably, the reactions of **10a–c** with EDA catalyzed by [Ru(CO)(ttppp)] (0.1 mol %) gave **11a–c** in 81–88 % yields, higher than the 75 and 57 % yields obtained for **11a** and **11b**, respectively, by using a silver(I) catalyst (2.5 mol %).[24d] In the [Ru(CO)(ttppp)]-catalyzed reactions, the yield ratios of **11**:**8** reach up to 25:1.

In conclusion, we have determined the crystal structures of a reactive M=$CHCO_2Et$ species and a *trans*-[M(CHR)(CO)] species. Both species are kinetically stabilized by Suslick's bis-pocket porphyrin ttppp. This sterically encumbered porphyrin ligand also has a significant impact on the chemoselectivity in [Ru(CO)(por)]-catalyzed reactions of EDA. The isolation of **2** and **3** implies that *trans*-[M($CHCO_2Et$)(CO)(por)] could be an intermediate in [M(CO)(por)]-catalyzed carbenoid transfer reactions. Such intermediates have not been structurally characterized previously; a related model complex, *trans*-[Ru(NSO_2R)(CO)(por)], with a long Ru−N(nitrene) bond has been reported in our recent DFT calculation on [Ru(CO)(por)]-catalyzed intermolecular nitrene transfer reactions.[25] The present work provides useful information on the mechanism of C−C

Table 3. Comparison of the catalytic properties of [Ru(CO)(ttppp)] and [Ru(CO)(tmp)] in the treatment of allyl halides (**10**) with EDA.[a]



			[Ru(CO)(ttppp)]			[Ru(CO)(tmp)]		
Entry	Allyl halide	Product	Yield of **11**[b] [%]	**11**:**8**[c]	*cis*/*trans* (**8**)[c]	Yield of **11**[b] [%]	**11**:**8**[c]	*cis*/*trans* (**8**)[c]
1	 **10a**	 **11a**	88	25:1	*cis* only	13	0.43:1	1:0.5
2	 **10b**	 **11b**	81	12:1	1:0.07	6	0.15:1	1:0.32
3	 **10c**	 **11c**	84 (1:1)	16:1	1:0.05	6	0.18:1	1:0.38

[a] Reaction conditions: **10** (1 mL), EDA (1.0 mmol), catalyst (0.001 mmol), RT. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy.

bond formation reactions with diazo compounds catalyzed by carbonyl metalloporphyrins.[4f]

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Keywords: carbenoids • porphyrinoids • reactive intermediates • ruthenium • structure elucidation

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