ELSEVIER

Coordination Chemistry Reviews 231 (2002) 151–164

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

# Ruthenium and osmium porphyrin carbene complexes: synthesis, structure, and connection to the metal-mediated cyclopropanation of alkenes

Chi-Ming Che *, Jie-Sheng Huang

*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

Received 6 November 2001; received in revised form 1 February 2002

## Contents

## Abstract

A series of monocarbene ruthenium/osmium porphyrins [M(Por)(CRR′)] (M = Ru, Os; R=R′ in some cases) and two biscarbene osmium porphyrins $[Os(Por)(CR_2)_2]$ have been prepared by several research groups from reactions of diazo compounds with ruthenium/osmium porphyrins $[M(Por)]_2$, [M(Por)(CO)] (M = Ru, Os), [Ru(Por)], or $[Os(Por)(CR_2)]$, or from reactions of $K_2[Ru(Por)]$ with germinal dihalides. The structures of [Os(TTP)(CRR′)(THF)] ($CRR' = C(p\text{-}C_6H_4CH_3)_2$, $CHSiMe_3$), $[Ru(TPP)(C(CO_2Et)_2)(MeOH)]$, [Ru(Por*)(CRR′)] ($CRR' = CPh_2$, $C(Ph)CO_2CH_2CH{=}CH_2$), $[Os(TPFPP)(CPh_2)(MeOH)]$, and $[Os(TPFPP)(CPh_2)_2]$ have been determined by X-ray crystallography, which feature M=C(carbene) bond lengths of 1.79(2)–1.870(2) Å for the monocarbene complexes and 2.035(2), 2.027(3) Å for the biscarbene complex. Reactions of [Os(TTP)(CHR)] ($R = CO_2Et$, $SiMe_3$) with *para*-substituted pyridines $4\text{-}X\text{-}C_5H_4N$ afford osmium porphyrin ylide complexes $[Os(TTP)(CH(R)(4\text{-}X\text{-}C_5H_4N))(4\text{-}X\text{-}C_5H_4N)]$. The complexes $[Os(TTP)(CHCO_2Et)]$, $[Ru(TPP)(C(CO_2Et)_2)]$, and $[Os(TPFPP)(CPh_2)_2]$ all undergo cyclopropanation reactions with styrene. The biscarbene complex $[Os(TPFPP)(CPh_2)_2]$ also reacts with unfunctionalized alkenes such as cyclohexene to yield C–H insertion products. A few ruthenium/osmium porphyrin carbene complexes, including $[Os(TTP)(CHCO_2Et)]$, $[Ru(TPP)(CHCO_2Et)]$, [Ru(Por*)(CHX)(L)] ($X = CO_2R$, $CO_2CH_2CH{=}CR^cR^t$; L = a ligand with considerable *trans* effect such as CHX), and $[Os(TPFPP)(CPh_2)_2]$, are proposed to be the active intermediates in the corresponding ruthenium/osmium porphyrin-catalyzed alkene cyclopropanations. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Metal–carbene complexes; Ruthenium and osmium porphyrins; Metal-catalyzed cyclopropanations

---

* Corresponding author. Tel.: +852-2859-2154; fax: +852-2857-1586
*E-mail address:* cmche@hku.hk (C.-M. Che).

PII: S0010-8545(02)00117-0

## 1. Introduction

In 1977 (some 13 years after the discovery of the first transition metal carbene complex), Mansuy et al. reported the formation of the first metalloporphyrin carbene complex [Fe(TPP)($CCl_2$)] (from reaction of [Fe(TPP)] with $CCl_4$ in the presence of reducing agents) [1], which well mimics the formation of carbene complexes of cytochrome P-450 on reduction of various polyhalogenated compounds. Three years later, Callot and Piechocki found that rhodium porphyrins catalyze the cyclopropanation of alkenes with ethyl diazoacetate to form cyclopropyl esters in 60–71% yields with a striking *cis*-selectivity [2]; the *cis*-selectivity can be rationalized by the intermediacy of rhodium porphyrin carbene species in the catalytic processes. These works first demonstrate the close relevance of metalloporphyrin carbene complexes to both biological systems and metal-catalyzed organic reactions. Up to now, the halocarbene iron porphyrins have been extensively studied by Mansuy and co-workers [3–7], whereas the rhodium porphyrin-catalyzed alkene cyclopropanations have been dramatically enriched by Kodadek and co-workers (from the development of asymmetric alkene cyclopropanation to detailed mechanistic studies) [8–13].

Ruthenium and osmium porphyrin carbene complexes were first synthesized by the groups of Collman (in 1985) [14] and Woo (in 1992) [15], respectively. The complexes [Ru(Por)(CHR)] prepared by Collman et al. are the first metalloporphyrins with α-hydrogen atoms in the carbene ligands, whereas the complex [Os(TTP)($CHCO_2Et$)] prepared by Woo and co-workers is the first isolated metal carbene complex that shows catalytic cyclopropanation activity [16]. Recently, the groups of Simonneaux [17,18], Che [19,20], Bekessel [21], and Gross [22] reported the asymmetric cyclopropanation of alkenes with alkyl diazoacetates catalyzed by chiral ruthenium porphyrins, which afford the optically-active cyclopropyl esters (probably via ruthenium porphyrin carbene intermediates) in up to quantitative yield and 98% ee with high *trans–cis* ratios and catalyst turnovers. Che and co-workers also isolated a biscarbene osmium porphyrin, [Os(TPFPP)($CPh_2$)$_2$], which is the first isolated biscarbene metal complex that exhibits alkene cyclopropanation reactivity [23].

This review is focused on the carbene complexes of ruthenium and osmium porphyrins, with particular reference to their connections to ruthenium and osmium porphyrin-mediated alkene cyclopropanation reactions. Almost all the porphyrin ligands involved here are *meso*-tetraarylporphyrinato dianions, whose structures, together with their abbreviations, are depicted in Figs. 1 and 2.

## 2. Synthesis and spectral features of ruthenium and osmium porphyrin carbene complexes

### 2.1. Synthesis

### 2.1.1. Monocarbene complexes

Treatment of diruthenium porphyrin [Ru(TTP)]$_2$ with ethyl diazoacetate $N_2CHCO_2Et$ and diazoethane $N_2CHCH_3$ affords [Ru(TTP)($CHCO_2Et$)] and [Ru(TTP)($CHCH_3$)], respectively [14] (reaction (1) in Fig. 3). This method applies to osmium analogues as well: the reactions between [Os(TTP)]$_2$ and diazo compounds $N_2CHCO_2Et$, $N_2C(p\text{-}C_6H_4CH_3)_2$, $N_2CHSiMe_3$, and $N_2C(CO_2Et)_2$ produce the corresponding osmium porphyrin carbene complexes [Os(TTP)($CHCO_2Et$)], [Os(TTP)($C(p\text{-}C_6H_4CH_3)_2$)], [Os(TTP)($CHSiMe_3$)], and [Os(TTP)($C(CO_2Et)_2$)] in 77–96% yields [15,24].

Reaction (1) is not applicable for preparation of ruthenium or osmium porphyrins with sterically encumbered porphyrin ligands such as TMP, which does not lead to formation of a stable diruthenium porphyrin [Ru(TMP)]$_2$. The complex [Ru(TMP)($CHCO_2Et$)] was prepared from reaction of the monomer [Ru(TMP)] with $N_2CHCO_2Et$ [25] (reaction (2) in Fig. 3). An alternative mononuclear precursor to ruthenium porphyrin carbene complexes is the ruthenium porphyrin dianion $K_2$[Ru(TTP)], which reacts with germinal dihalides $Cl_2CHCH_3$ and $Cl_2CHSiMe_3$ to form [Ru(TTP)($CHCH_3$)] and [Ru(TTP)($CHSiMe_3$)] [26] (reaction (3) in Fig. 3).

The most convenient method of preparing ruthenium and osmium carbene porphyrins is from the reaction of carbonyl complexes [Ru(Por)(CO)] and [Os(Por)(CO)] with diazo compounds, as shown in reaction (4) in Fig. 3. Treatment of [Ru(Por*)(CO)(EtOH)] with $N_2CHCO_2Et$ generates [Ru(Por*)($CHCO_2Et$)] in situ [19]. The reaction of [Ru(TPP)(CO)(EtOH)] with $N_2C(CO_2Et)_2$ leads to isolation of [Ru(TPP)-($C(CO_2Et)_2$)] in 64% yield [27]. The first osmium porphyrin carbene complex prepared from reaction (4) is [Os(TPFPP)($CPh_2$)], which was obtained in 92% yield by treating [Os(TPFPP)(CO)] with $N_2CPh_2$ [23]. Other ruthenium and osmium porphyrin carbene complexes prepared according to reaction (4) include [Ru(Por*)($CPh_2$)], [Ru(Por*)($C(Ph)CO_2CH_2CH{=}CH_2$)] [20], [Ru(TPFPP)($CPh_2$)], [Ru(TPFPP)($C(Ph)CO_2$-$CH_2CH{=}CH_2$)], and [Os(3,4,5-MeO–TPP)($CPh_2$)] [28].

### 2.1.2. Biscarbene complexes

Reaction of [Os(TTP)($C(p\text{-}C_6H_4CH_3)_2$)] with excess $N_2C(p\text{-}C_6H_4CH_3)_2$ gives rise to [Os(TTP)($C(p\text{-}C_6H_4CH_3)_2$)$_2$] [15] (reaction (5) in Fig. 4). This biscarbene osmium porphyrin has not been isolated in pure form, but was always contaminated by the monocarbene complex [Os(TTP)($C(p\text{-}C_6H_4CH_3)_2$)]. A pure biscarbene

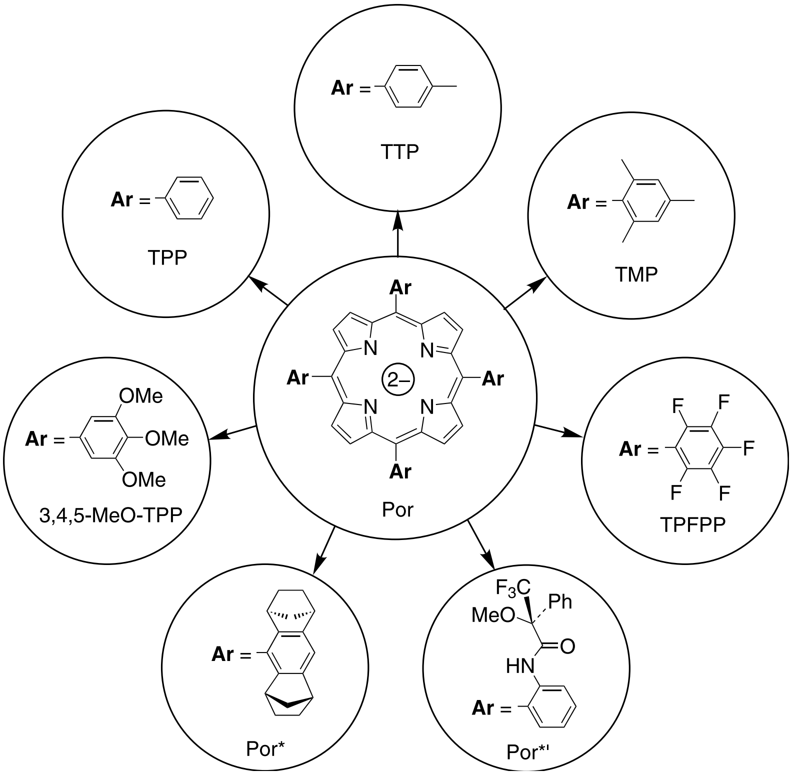


Fig. 1. Schematic structures of *meso*-tetraarylporphyrin ligands TPP, TTP, TMP, 3,4,5-MeO–TPP, TPFPP, Por*, and Por*′.

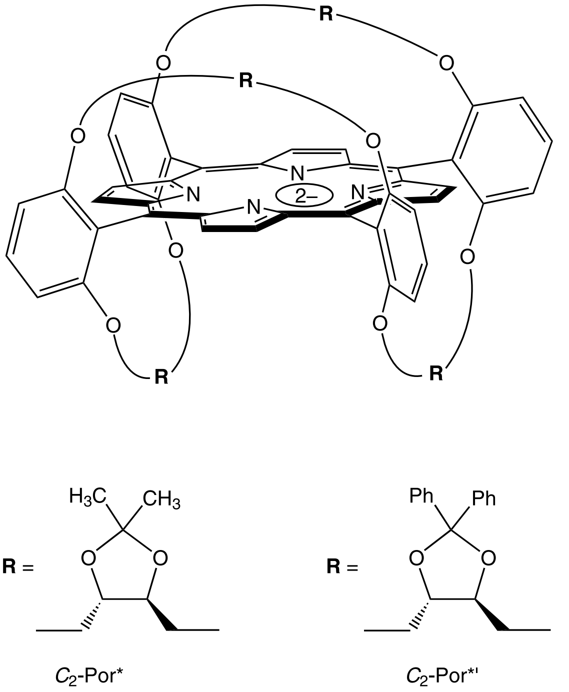


Fig. 2. Schematic structures of *meso*-tetraarylporphyrin ligands $C_2$–Por* and $C_2$–Por*′.

osmium porphyrin, [Os(TPFPP)$(CPh_2)_2$], was isolated from treatment of [Os(TPFPP)$(CPh_2)$] with excess $N_2CPh_2$ [23]. The biscarbene complex [Os(TPFPP)-$(CPh_2)_2$] can also be prepared in a similar yield from

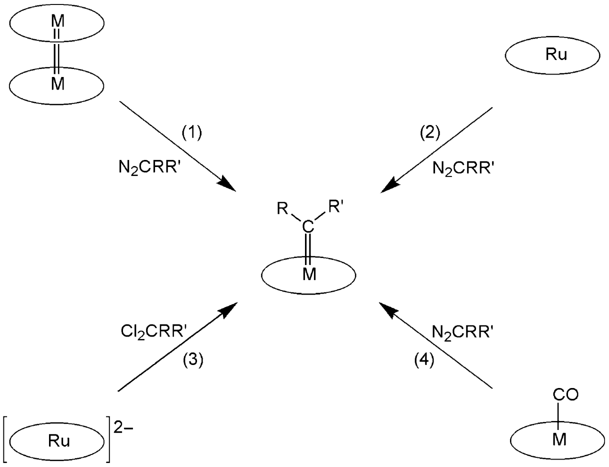


Fig. 3. Syntheses of monocarbene ruthenium and osmium porphyrins. Note that in some cases R and R′ are identical.

direct reaction of [Os(TPFPP)(CO)] with excess $N_2CPh_2$ (reaction (6) in Fig. 4). Complexes [Os(TTP)$(C(p\text{-}C_6H_4CH_3)_2)_2$] and [Os(TPFPP)$(CPh_2)_2$] are so far the only examples of a well-characterized biscarbene metalloporphyrin.

## 2.2. *Spectral features*

All the known ruthenium and osmium porphyrin carbene complexes are diamagnetic species. This facilitates their characterization by NMR spectroscopy. The

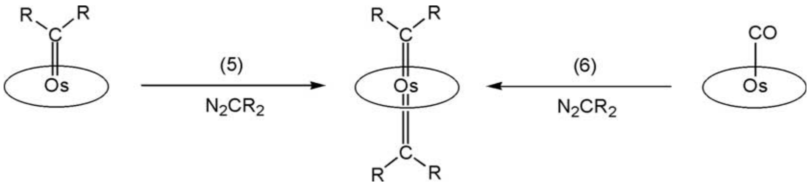


Fig. 4. Syntheses of biscarbene osmium porphyrins.

following NMR signals are considered as distinctive spectral features of the carbene axial ligands in diamagnetic ruthenium and osmium porphyrin carbene complexes: (i) The $^{13}$C-NMR signal of the M=C carbon, which usually appears at $\delta > 200$; (ii) The $^{1}$H-NMR signal of the M=$CH$R proton, which usually appears at $\delta > 13$.

Table 1 shows the $^{1}$H- and $^{13}$C-NMR spectral data for the ruthenium and osmium porphyrin carbene complexes reported in the literature. The pyrrole proton resonances of the porphyrin ring ($H_\beta$) appear as a multiplet (with a pattern resembling that of an AB system) for either [Ru(Por*)(CPh$_2$)] or [Ru(Por*)-(C(Ph)CO$_2$CH$_2$CH=CH$_2$)] and as a singlet for each of the other complexes, similar to those of the carbonyl ruthenium and osmium complexes [Ru(Por)(CO)] and [Os(Por)(CO)] bearing the same porphyrin ligand. Owing to C–H coupling, the complexes with monosubstituted carbene ligands CHR each give the $^{13}$C-NMR signal of the M=C carbon as a doublet, in contrast to the singlet observed for the corresponding carbon in the complexes with doubly substituted carbene ligands.

Examination of the NMR data in Table 1 reveals a marked dependence of the spectral data on the deuterated solvent employed (for example, the $H_\beta$ chemical shifts are considerably larger in $C_6D_6$ than in THF-$d_6$ or $CDCl_3$). Also, the $H_\beta$ and M=CH– signals of the ruthenium carbene complexes are far downfield and upfield, respectively, from the corresponding signals of the osmium carbene complexes. Furthermore, the $^{13}$C-NMR chemical shifts of the M=C carbons fall into a rather wide range of $\delta$ 211.6–315; for a given M–Por–CR$_2$ combination, the M=C signal of the biscarbene complex is substantially downfield from that of the monocarbene counterpart.

The UV–vis spectral data (which are shown in Table 1 as well) of some reported ruthenium and osmium porphyrin monocarbene complexes resemble those of corresponding carbonyl ruthenium and osmium porphyrins [Ru(Por)(CO)] and [Os(Por)(CO)] (compare, for example, the Soret and $\beta$ bands of [Ru(TTP)(CH-CO$_2$Et)] (409 and 529 nm) and [Ru(TTP)(CO)] (414 and 532 nm) [29]), or those of [Os(TPFPP)(CPh$_2$)] (405 and 516 nm) and [Os(TPFPP)(CO)] (399 and 511 nm) [23]). Conversion of the monocarbene complex [Os(TPFPP)(CPh$_2$)] to the biscarbene complex [Os(TPFPP)(CPh$_2$)$_2$] results in an appreciable red shift for both the Soret and $\beta$ bands (see Table 1). Note that there seem to be two Soret bands in the spectrum of [Ru(TTP)(CHCH$_3$)] or [Ru(Por*)(CPh$_2$)], which are different from the single Soret band observed for the majority of the ruthenium and osmium porphyrin

Table 1
Key spectral data of ruthenium and osmium porphyrin carbene complexes

| Complex | $^{1}$H-NMR | | $^{13}$C-NMR | UV–vis $\lambda_{max}$(log $\varepsilon$) (nm) | Reference |
|---|---|---|---|---|---|
| | $\delta$($H_\beta$) | $\delta$(M=CH–) | $\delta$(M=C) | | |
| [Ru(TTP)(CHCO$_2$Et)] [a] | 8.78 (s) | 13.43 | | 409 (4.96), 529 (4.02) | [14] |
| [Ru(TTP)(CHCH$_3$)] [a] | 8.73 (s) | 13.03 | | 395 (4.82), 421 (4.97), 527 (4.14) | [14] |
| [Ru(TTP)(CHSiMe$_3$)] [b] | 8.21 (s) | 19.44 | | 408 (5.24), 527 (4.15) | [26] |
| [Ru(TMP)(CHCO$_2$Et)] [a] | 8.55 (s) | 13.79 | | 404 (Soret), 525 (v br) | [25] |
| [Ru(TPP)(C(CO$_2$Et)$_2$)] [c] | 8.56 (s) | | 271.36 (s) | 406 (5.10), 531 (4.11) | [27] |
| [Ru(Por*)(CPh$_2$)] [c] | 8.26 (m) | | 315 (s) | 397 (5.19), 432 (5.06), 536 (4.29) | [20] |
| [Ru(Por*)(C(Ph)CO$_2$CH$_2$CH=CH$_2$)] [c] | 8.35 (m) | | 285 (s) | 402 (5.26), 442 sh (4.72), 533 (4.20) | [20] |
| [Os(TTP)(CHCO$_2$Et)] [a] | 8.35 (s) | 21.60 | 211.6 (d) | 398, 408 | [15] |
| [Os(TTP)(CHSiMe$_3$)] [a] | 8.01 (s) | 28.95 | 295.5 (d) | 388, 420 | [15] |
| [Os(TTP)(C($p$-C$_6$H$_4$CH$_3$)$_2$)] [a] | 8.15 (s) | | 264.6 (s) | 410 (Soret), 522, 548 | [15] |
| [Os(TTP)(C(CO$_2$Et)$_2$)] [a] | 8.45 (s) | | | 398 (Soret) | [24] |
| [Os(TPFPP)(CPh$_2$)] [c] | 7.73 (s) | | 273.60 (s) | 380 sh, 405 (Soret), 516, 545 | [23] |
| [Os(TTP)(C($p$-C$_6$H$_4$CH$_3$)$_2$)$_2$] [a] | 8.63 (s) | | 305.5 | | [15] |
| [Os(TPFPP)(CPh$_2$)$_2$] [c] | 8.26 (s) | | 313.79 | 380 sh, 410 (Soret), 543 | [23] |

[a] In $C_6D_6$ (NMR) or $C_6H_6$ (UV–vis).
[b] In THF-$d_8$ (NMR) or THF (UV–vis).
[c] In $CDCl_3$ (NMR) or $CH_2Cl_2$ (UV–vis).

carbene complexes. In general, metalloporphyrins exhibiting two Soret bands are rare; of previous examples are a few osmium porphyrins with nitrido or nitrosyl axial ligands [30].

Mass spectrometry has been used as an additional spectroscopic method for characterization of [Ru(Por*)($CPh_2$)], [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] [20], [Os(TTP)(C(*p*-$C_6H_4CH_3)_2$)] [15], [Os(TTP)-(C($CO_2Et)_2$)] [24], [Os(TPFPP)($CPh_2$)] [23], and [Os(TPFPP)($CPh_2)_2$] [23]. The parent ions of these complexes, either monocarbene or biscarbene species, are sufficiently stable to be detected by employing FAB or EI mass spectrometers.

## 3. Structure of ruthenium and osmium porphyrin carbene complexes

Quite a few ruthenium and osmium porphyrin carbene complexes have been characterized by X-ray structure determination, all of which except [Os(TTP)($CHSiMe_3$)] contain disubstituted carbene ligands. When crystallizing from solutions containing coordinating molecules such as methanol and tetrahydrofuran, the monocarbene complexes usually bind the coordinating molecules at the axial sites *trans* to the carbene ligands. The key bond lengths and angles observed in the crystal structures of ruthenium and osmium porphyrin carbene complexes are summarized in Table 2.

The ditolylcarbene complex [Os(TTP)(C(*p*-$C_6H_4CH_3)_2$)(THF)] and the trimethylsilyl-carbene complex [Os(TTP)($CHSiMe_3$)(THF)] reported by Woo and co-workers in 1994 [31] are the first examples of structurally characterized osmium porphyrin carbene complexes. Both complexes have a six-coordinate osmium center embedded in a basically planar porphyrin ring, with the osmium atom slightly out of the porphyrin plane toward the carbene ligand (0.14 and 0.22 Å for the ditolyl- and trimethylsilyl-carbene complexes, respectively). The Os=C(carbene) bond length in the ditolylcarbene complex is 1.865(5) Å, which is longer than that of 1.79(2) Å in the trimethylsilyl-carbene complex.

The first structurally characterized ruthenium porphyrin carbene complex is the di(ethoxycarbonyl)carbene complex [Ru(TPP)(C($CO_2Et)_2$)(MeOH)] reported by Simonneaux and co-workers in 1998 [27]. This ruthenium carbene complex also has a six-coordinate metal center embedded in a basically planar porphyrin ring, like the foregoing ditolyl- and trimethylsilyl-carbene osmium porphyrins. The ruthenium atom is 0.12 Å out of the porphyrin plane toward the carbene ligand. The Ru=C(carbene) bond length (1.829(9) Å) and the $EtO_2C{-}C{-}CO_2Et$ angle (112.2(7)°) are similar to the Os=C(carbene) bond length (1.865(5) Å) and the tolyl–C–tolyl angle (113.0(4)°), respectively, in the ditolylcarbene osmium porphyrin [Os(TTP)(C(*p*-$C_6H_4CH_3)_2$)(THF)].

Complexes [Ru(Por*)($CPh_2$)] and [Ru(Por*)-(C(Ph)$CO_2CH_2CH{=}CH_2$)] recently reported by Che et al. [20] are the first examples of a chiral metalloporphyrin carbene complex. Figs. 5 and 6 show the crystal structures of the diphenylcarbene complex [Ru(Por*)-($CPh_2$)] and the (allyloxycarbonyl)phenylcarbene complex [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)], respectively. Although both the diphenyl- and (allyloxycarbonyl)phenyl-carbene complexes were crystallized from solvents containing coordinating molecules (acetonitrile or water), each of them has a five-coordinate ruthenium center, in contrast to the six-coordinate rutheium/osmium centers in the ditolyl-, di(ethoxycarbonyl)-, and trimethylsilyl-carbene ruthenium/osmium porphyrins described above. However, the M=CRR′ bond lengths and the R–C–R′ angles in all these five- and six-coordinate ruthenium/osmium porphyrin carbene complexes are similar. The porphyrin rings in [Ru(Por*)($CPh_2$)] and [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] are appreciably puckered and the ruthenium atoms in the two complexes are ca. 0.2 Å out of the mean plane of the four pyrrole nitrogen atoms toward the carbene ligand. Replacing one of the phenyl groups in the diphenylcarbene ligand of [Ru(Por*)($CPh_2$)] by an allyloxycarbonyl group to form [Ru(Por*)(C(Ph)-

Table 2

Structurally characterized monocarbene ruthenium/osmium porphyrins [M(Por)(CRR′)(L)] (M = Ru, Os) and biscarbene osmium porphyrin [Os(TPFPP)(CRR′)$_2$] (R = R′ = Ph)

| Complex | L | M=CRR′ (Å) | R–C–R′ (°) | M–O(L) (Å) | Reference |
|---|---|---|---|---|---|
| [Os(TTP)(C(*p*-$C_6H_4CH_3)_2$)(THF)] | THF | 1.865(5) | 113.0(4) | 2.328(3) | [31] |
| [Os(TTP)($CHSiMe_3$)(THF)] | THF | 1.79(2) | | 2.43(2) | [31] |
| [Ru(TPP)(C($CO_2Et)_2$)(MeOH)] | MeOH | 1.829(9) | 112.2(7) | 2.293(6) | [27] |
| [Os(TPFPP)($CPh_2$)(MeOH)] | MeOH | 1.870(2) | 112.3(2) | 2.347(2) | [23] |
| [Ru(Por*)($CPh_2$)] | | 1.860(6) | 112.1(5) | | [20] |
| [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] | | 1.847(3) | 114.3(2) | | [20] |
| [Os(TPFPP)($CPh_2)_2$] | | 2.035(2) 2.027(3) | 112.2(2) 111.7(2) | | [23] |

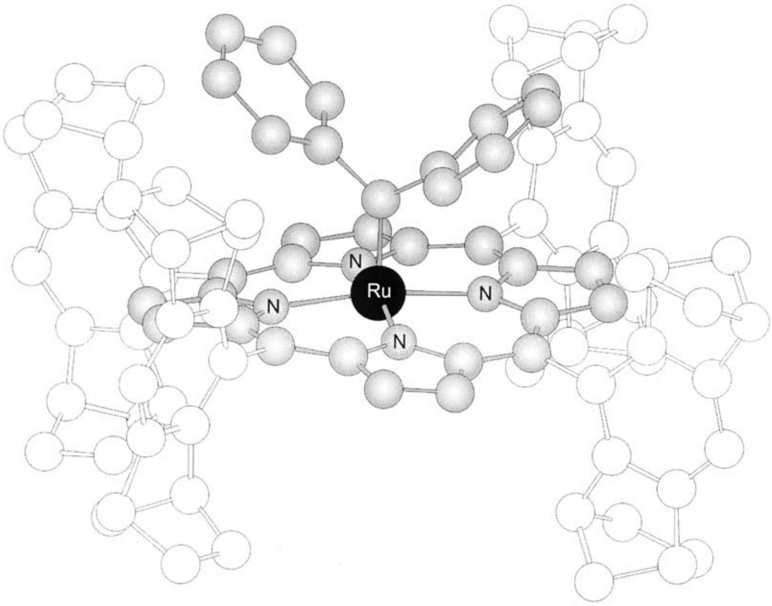


Fig. 5. Crystal structure of [Ru(Por*)($CPh_2$)] with omission of hydrogen atoms. For clarity, the atoms in the diphenylcarbene ligand and the porphyrin ring were filled with gray colors.

$CO_2CH_2CH{=}CH_2$)] (the first metalloporphyrin carbene complex with a pendant alkene double bond in the carbene ligand) significantly increases the steric interaction between the carbene ligand and the norbornane moieties of the Por* ligand. For example, the norbornane moieties adjacent to the (allyloxycarbonyl)phenylcarbene ligand in [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] are severely distorted from the orientations basically perpendicular to the porphyrin ring [20].

The bis(diphenylcarbene)osmium porphyrin [Os(TPFPP)($CPh_2$)$_2$], again recently reported by Che and co-workers [23], is hitherto the only example of a

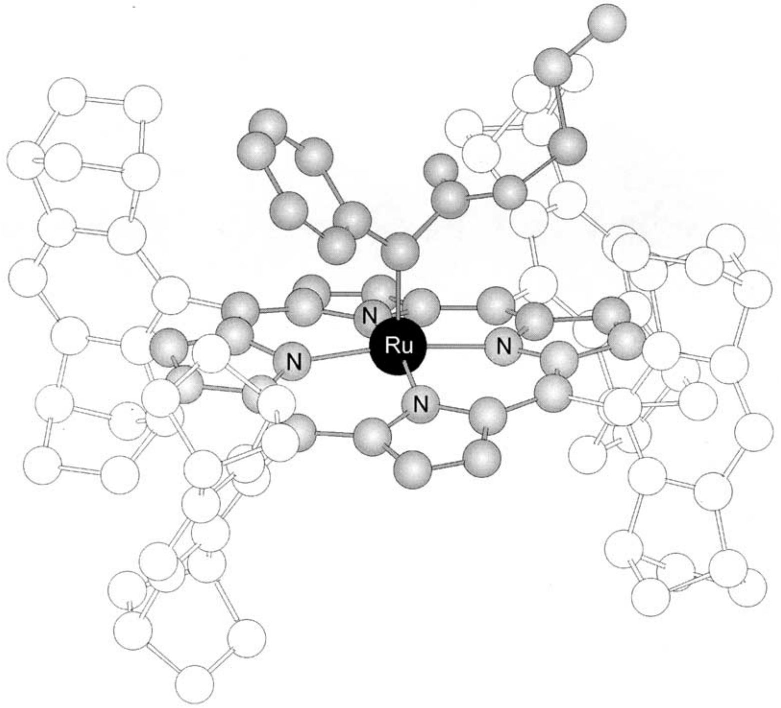


Fig. 6. Crystal structure of [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] with omission of hydrogen atoms. For clarity, the atoms in the (allyloxycarbonyl)phenylcarbene ligand and the porphyrin ring were filled with gray colors.

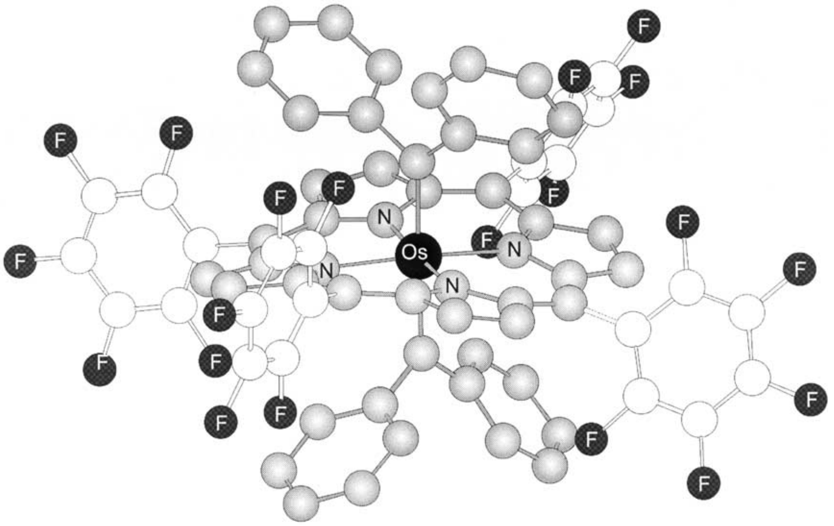


Fig. 7. Crystal structure of [Os(TPFPP)$(CPh_2)_2$] with omission of hydrogen atoms. For clarity, the atoms in the diphenylcarbene ligands and the porphyrin ring were filled with gray colors.

structurally characterized biscarbene metalloporphyrin. The crystal structure of this biscarbene complex (Fig. 7) exhibits several unusual features. One is that the Os=C(carbene) bonds (2.035(2) and 2.027(3) Å) are much longer than those of the monocarbene ruthenium and osmium porphyrins. Further, the two *trans* carbene axial ligands are roughly perpendicular, unlike the parallel *trans* carbene groups in an octahedral *trans*-biscarbene molybdenum complex [32]. Moreover, the TPFPP ligand in [Os(TPFPP)$(CPh_2)_2$] is significantly ruffled (mean deviation from the least-squares plane: 0.197 Å), in contrast to the basically planar TPFPP ligand in the monocarbene complex [Os(TPFPP)-$(CPh_2)$–(MeOH)] [23] (Fig. 8).

## 4. Reactivity of ruthenium and osmium porphyrin carbene complexes

### 4.1. Reaction with phosphine and pyridine derivatives

Collman et al. reported that treatment of the ruthenium (ethoxycarbonyl)carbene complex [Ru(OEP)(CH-$CO_2Et$)] (OEP = octaethylporphyrinato dianion) with 1 equivalent of triphenylphosphine transforms the complex to [Ru(OEP)$(PPh_3)$] [25]. The organic products in the reaction are diethyl maleate and fumarate arising from the coupling of the (ethoxycarbonyl)carbene groups.

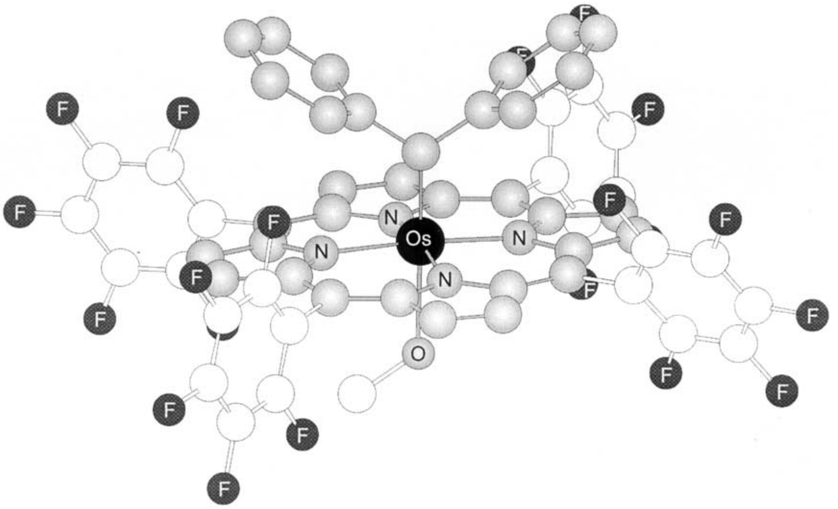


Fig. 8. Crystal structure of [Os(TPFPP)$(CPh_2)$(MeOH)] with omission of hydrogen atoms. For clarity, the atoms in the diphenylcarbene ligand and the porphyrin ring were filled with gray colors.

Woo and co-workers investigated the reactions between monocarbene osmium porphyrins and pyridine derivatives [24]. They found that complexes [Os(TTP)($CHCO_2Et$)] and [Os(TTP)($CHSiMe_3$)] bearing monosubstituted carbene ligands can react with *para*-substituted pyridines 4-X–$C_5H_4N$ to form osmium porphyrin ylide complexes. For example, reaction of the (ethoxycarbonyl)carbene complex [Os(TTP)($CHCO_2Et$)] with 4-X–$C_5H_4N$ (X = Me, *i*Pr, $NMe_2$) affords stable osmium ylide complexes [Os(TTP)(CH($CO_2Et$)(4-X–$C_5H_4N$))(4-X–$C_5H_4N$)] (reaction (7) in Fig. 9). The ylide complexes with X = Me and *i*Pr are reactive toward styrene cyclopropanation, affording a mixture of *trans* and *cis* ethyl 2-phenylcyclopropane-1-carboxylate in up to 95% yields with up to 28:1 *trans–cis* ratios. In the case of the (trimethylsilyl)carbene complex [Os(TTP)($CHSiMe_3$)], its reaction with 4-Me–$C_5H_4N$ results in an equilibrium formation of [Os(TTP)($CHSiMe_3$)(4-Me–$C_5H_4N$)] and the osmium ylide complex [Os(TTP)(CH($SiMe_3$)(4-Me–$C_5H_4N$))(4-Me–$C_5H_4N$)]. However, complex [Os(TTP)(C($CO_2Et)_2$)] (which bears a disubstituted carbene ligand) does not react with 4-Me–$C_5H_4N$ to yield an osmium ylide complex. Prolonged reaction between [Os(TTP)(C($CO_2Et)_2$)] and 4-Me–$C_5H_4N$ produces mainly [Os(TTP)(4-Me–$C_5H_4N)_2$] (reaction (8) in Fig. 9).

### 4.2. Reaction with alkenes

Several ruthenium or osmium porphyrin carbene complexes, including [Os(TTP)($CHCO_2Et$)], [Ru(TPP)(C($CO_2Et)_2$)], and [Os(TPFPP)($CPh_2)_2$], have been found to be reactive toward alkenes. Reaction of the (ethoxycarbonyl)carbene complex [Os(TTP)($CHCO_2Et$)] with excess styrene affords a mixture of *trans* and *cis* ethyl 2-phenylcyclopropane-1-carboxylate in ca. 75% yield with a *trans–cis* ratio of 11.5:1 (reaction (9) in Fig. 10), as reported by Woo and co-workers [16]. The reaction between styrene and the di(ethoxycarbonyl)carbene complex [Ru(TPP)(C($CO_2Et)_2$)] reported by Simonneaux and co-workers [27] produces diethyl 2-phenylcyclopropane-1,1-dicarboxylate in 66% yield (reaction (10) in Fig. 10). Che and co-workers found that the biscarbene osmium porphyrin [Os(TPFPP)($CPh_2)_2$] can react with a series of aromatic alkenes including styrene and its derivatives to afford 1,1-diphenyl-2-arylcyclopropanes in 70–94% yields (reaction (11) in Fig. 10), accompanied by formation of the monocarbene osmium porphyrin [Os(TPFPP)($CPh_2$)] [23]. The reaction between the biscarbene osmium porphyrin with *trans*-β-methylstyrene is rather striking, which results in formation of the corresponding cyclopropane in 94% yield, in contrast to the poor cyclopropane yield observed for the cyclopropanation of the same alkene mediated by other metalloporphyrins.

Che and co-workers also found that the biscarbene osmium porphyrin [Os(TPFPP)($CPh_2)_2$] is reactive toward allylic alkenes, yielding C–H insertion products rather than cyclopropanes [23]. The reaction of [Os(TPFPP)($CPh_2)_2$] with cyclopentene and cyclohexene affords 3-diphenylmethyl cyclopentene and 3-diphenylmethyl cyclohexene in 80 and 83% yield, respectively, as

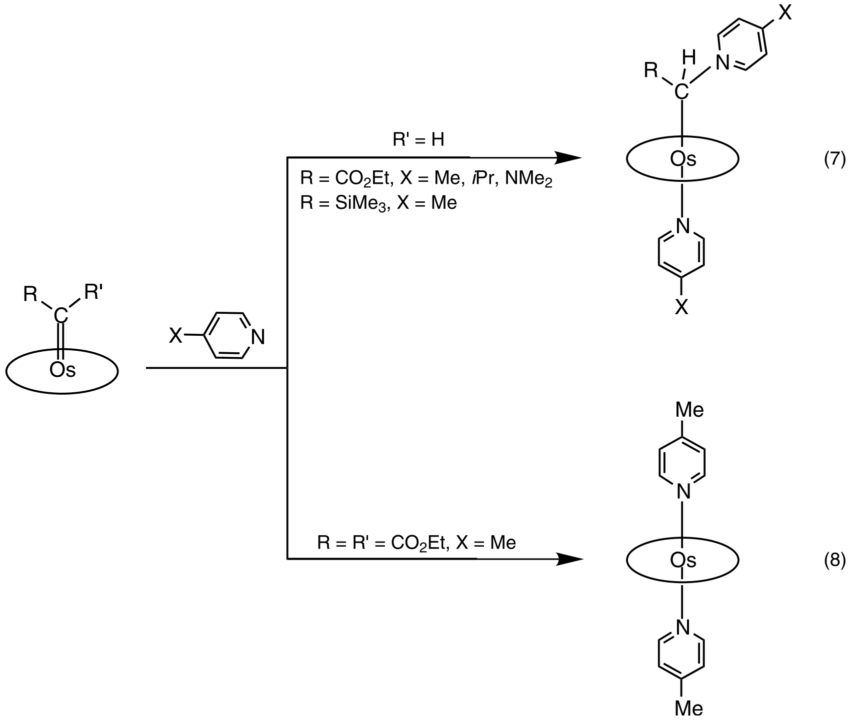


Fig. 9. Reactions of [Os(TTP)($CHCO_2Et$)], [Os(TTP)($CHSiMe_3$)], and [Os(TTP)(C($CO_2Et)_2$)] with *para*-substituted pyridines.

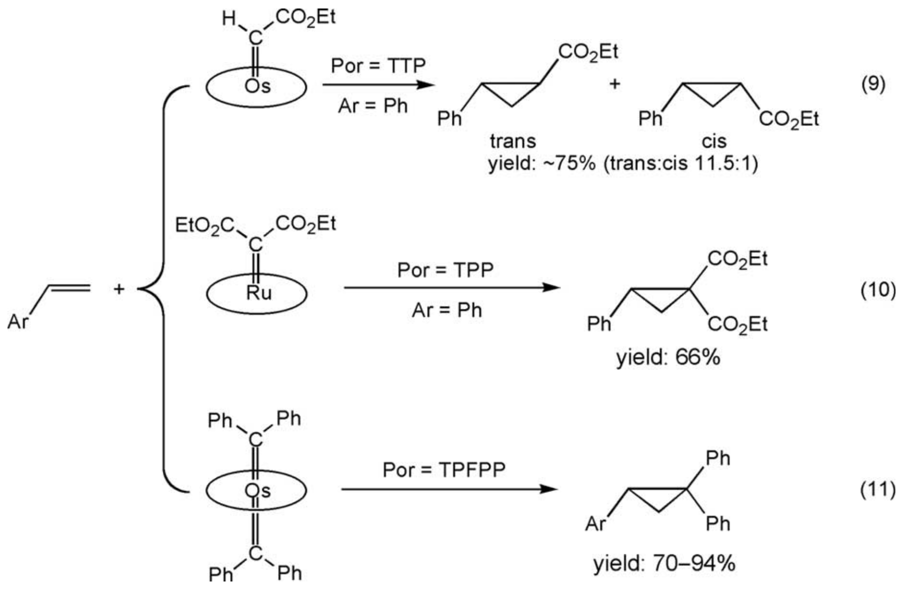


Fig. 10. Reactions of [Os(TTP)(CHCO$_2$Et)], [Ru(TPP)(C(CO$_2$Et)$_2$)], and [Os(TPFPP)(CPh$_2$)$_2$] with aromatic alkenes.

depicted in reactions (12) and (13) in Fig. 11. These are the first C–H insertion reactions between unfunctionalized alkenes and isolated metalloporphyrin carbene complexes.

## 5. Proposed ruthenium and osmium porphyrin carbene intermediates in metal-mediated cyclopropanation of alkenes

Metal-catalyzed cyclopropanation of alkenes with diazo compounds is a subject of numerous investigations [33,34]. Of the well-known such catalysts are the semicorrin-copper [35,36], bis(oxazoline)-copper [37–39], and ruthenium–pybox complexes [40–42] for intermolecular cyclopropanations (all are *trans*-selective) and the dirhodium carboxamidate complexes [43] for intramolecular cyclopropanations. These catalysts excellently effect asymmetric cyclopropanations and can all reach an enantiocontrol of $>90\%$ ee. A common drawback of them lies in the rather low catalyst turnover numbers in the catalytic processes (rarely larger than 100).

In contrast, metalloporphyrin cyclopropanation catalysts can reach thousands of catalyst turnovers, as first noted by Kodadek and co-workers in their studies of rhodium porphyrin cyclopropanation catalysts (all are *cis*-selective in intermolecular cyclopropanations as mentioned earlier) [8,10]. Reported ruthenium/osmium porphyrin cyclopropanation catalysts (all are *trans*-selective in intermolecular cyclopropanations) include [Os(TTP)(CO)(Py)], [Os(TTP)]$_2$, [Os(TTP)(CHCO$_2$Et)] [16], [Ru(TPP)(CO)], [Ru(TMP)(CO)] [17,19], [Ru(TMP)(O)$_2$], [Ru(Por*′)(O)$_2$] [17], [Ru(OEP)(CO)(EtOH)] [19], [Ru(Por*)(CO)(EtOH)] [19,20], [Ru(Por*)(CO)] [21], [Ru($C_2$–Por*)(CO)] [18,22], [Ru(TPP)(C(CO$_2$Et)$_2$)] [27], [Ru($C_2$–Por*′)(CO)] [22], [Ru(MPIXDME)(CO)] (MPIXDME = mesoporphyrin IX dimethyl ester dianion) [44], [Ru(Por*)(CPh$_2$)] [20], and [Os(TPFPP)(CO)] [23]. Some of the results for the cyclopropanation of styrene with ethyl diazoacetate catalyzed by these catalysts are shown in Table 3. The ruthenium porphyrin catalyst [Ru(Por*)(CO)(EtOH)] reported by Che and co-workers gives the highest trans–cis ratio of 36:1 (with the *trans* isomer formed in 98% ee), which is much higher than the trans–cis

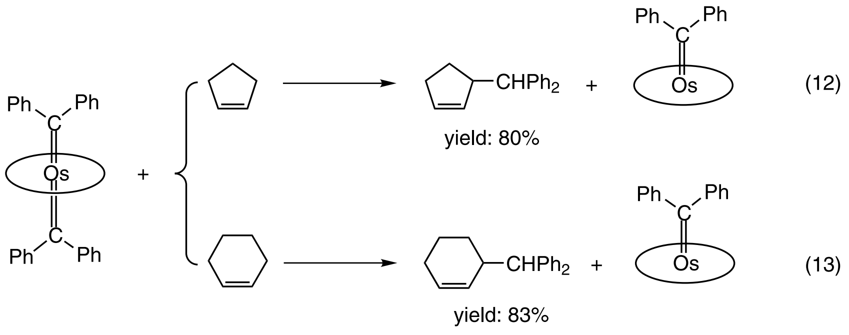
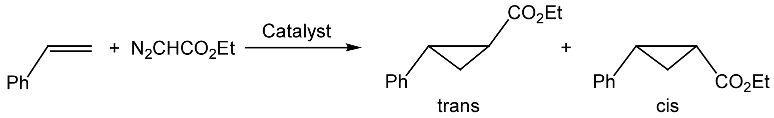


Fig. 11. Reactions of [Os(TPFPP)(CPh$_2$)$_2$] with allylic alkenes.

Table 3
Selected examples of intermolecular cyclopropanation of styrene with ethyl diazoacetate catalyzed by ruthenium and osmium porphyrins



| Catalyst | Reaction conditions | Yield (%) | trans–cis | ee (%) | | Reference |
|---|---|---|---|---|---|---|
| | | | | trans | cis | |
| [Os(TTP)(CO)(Py)] | Toluene, 22 °C, 2 h | 65 | 9.5:1 | | | [16] |
| [Os(TTP)]$_2$ | Toluene, 22 °C, 2 h | 79 | 10.2:1 | | | [16] |
| [Os(TTP)(CHCO$_2$Et)] | Toluene, 22 °C, 2 h | 63 | 8.9:1 | | | [16] |
| [Ru(TPP)(CO)] | r.t., 5 h | quant | 13:1 | | | [17] |
| [Ru(TMP)(CO)] | r.t., 5 h | quant | 7.9:1 | | | [17] |
| [Ru(TMP)(O)$_2$] | r.t., 5 h | quant | 7.1:1 | | | [17] |
| [Ru(Por*′)(O)$_2$] | r.t., 5 h | | 9:1 | 14 | 34 | [17] |
| [Ru(Por*)(CO)(EtOH)] | CH$_2$Cl$_2$, r.t., 20 h | 83 | 18:1 | 87 | 4 | [19] |
| [Ru(Por*)(CO)(EtOH)] | CH$_2$Cl$_2$, $-40$ °C, 20 h | 52 | 36:1 | 98 | | [20] |
| [Ru(Por*)(CO)] | ClCH$_2$CH$_2$Cl, r.t., 2 h | quant | 24:1 | 87 | 15 | [21] |
| [Ru(Por*)(CO)] | ClCH$_2$CH$_2$Cl, 0 °C, 2 h | quant | 19:1 | 91 | 27 | [21] |
| [Ru(C$_2$–Por*)(CO)] | r.t., 8 h | 85 | 4.0:1 | 46 | | [18] |
| [Ru(C$_2$–Por*)(CO)] | r.t., 24 h | | 6.3:1 | 58 | 23 | [22] |
| [Ru(Por*)(CPh$_2$)] | CH$_2$Cl$_2$, r.t., 20 h | 36 | 11:1 | 83 | 7 | [20] |

ratios reported for semicorrin- and bis(oxazoline)-copper catalysts (trans–cis $<4$) [35–39] and ruthenium–pybox catalysts (trans–cis $\leq 16$) [40–42] for the same cyclopropanation reaction. The highest catalyst turnover number in the [Ru(Por*)(CO)(EtOH)]-catalyzed cyclopropanations is $1.1 \times 10^4$ [20]!

Che and co-workers also reported that [Os(TPFPP)(CO)] can catalyze cyclopropanation of styrene with diphenyldiazomethane, producing 1,1,2-triphenylcyclopropane in 85% yield [23] (Fig. 12). This is currently the only example of metalloporphyrin-catalyzed alkene cyclopropanations with a diaryldiazomethane.

Intramolecular cyclopropanation catalyzed by metalloporphyrins are exceedingly rare. The earliest example was reported by Kodadek and co-workers by employing a rhodium porphyrin [10], which affords an optically active bicyclic lactone in 10% ee. The only other examples are the [Ru(Por*)(CO)(EtOH)]-catalyzed intramolecular cyclopropanations of several allylic or homoallylic diazoacetates recently reported by Che et al. [20], which yield optically active lactones in up to 85% ee.

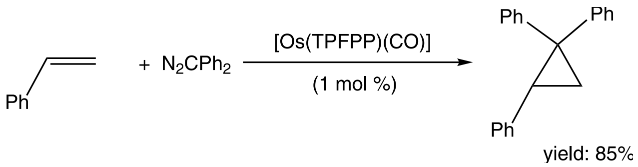


Fig. 12. Cyclopropanation of styrene with diphenyldiazomethane catalyzed by [Os(TPFPP)(CO)].

Almost all the above inter- and intramolecular alkene cyclopropanations catalyzed by ruthenium/osmium porphyrins are postulated to occur via ruthenium/osmium porphyrin carbene intermediates, as described below.

### 5.1. *Intermolecular cyclopropanation*

Woo and co-workers considered the monocarbene osmium porphyrin [Os(TTP)(CHCO$_2$Et)] as an important species in the catalytic cycle of the [Os(TTP)]$_2$-catalyzed cyclopropanations with N$_2$CHCO$_2$Et [16]. This is based on the fact that treatment of [Os(TTP)]$_2$ with N$_2$CHCO$_2$Et readily forms [Os(TTP)(CHCO$_2$Et)] [15], which can cyclopropanate styrene either stoichiometrically or catalytically, with stereoselectivities of organic products similar to those of the [Os(TTP)]$_2$-catalyzed cyclopropanations.

For the [Ru(TPP)(CO)]-catalyzed cyclopropanations, formation of monocarbene ruthenium porphyrin [Ru(TPP)(CHCO$_2$Et)] is a key step in the catalytic cycle postulated by Simonneaux and co-workers [44] (Fig. 13). This catalytic cycle features carbene transfer from [Ru(TPP)(CHCO$_2$Et)] to alkene followed by formation of a highly reactive bare ruthenium(II) complex [Ru(TPP)]. The bare ruthenium(II) complex then reacts with ethyl diazoacetate to regenerate the monocarbene species [Ru(TPP)(CHCO$_2$Et)]. Attack of alkene on the electrophilic carbene ligand in [Ru(TPP)(CHCO$_2$Et)] is assumed to be the rate-limiting step, which might lead to a three-center late transition state with a small cationic charge on the alkene double bond (see Fig. 14). This

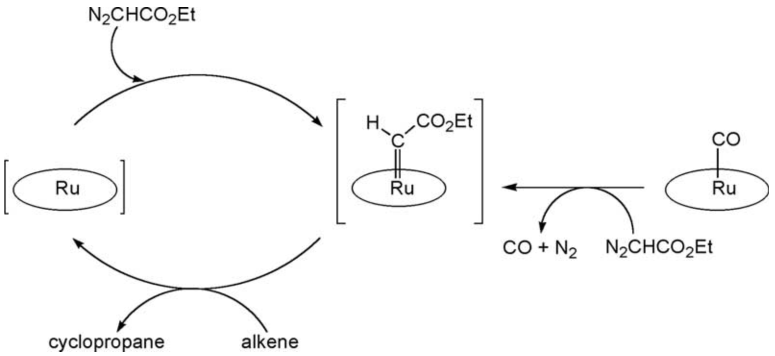


Fig. 13. Proposed catalytic cycle for [Ru(TPP)(CO)]-catalyzed cyclopropanation of alkenes with ethyl diazoacetate.

mechanism can rationalize why the [Ru(TPP)(CO)]-catalyzed cyclopropanations show higher reactivity for terminal alkenes or for the alkenes bearing electron-donating groups, and show higher trans–cis ratios but lower ratios of cyclopropanes versus carbene coupling products for the alkenes bearing electron-withdrawing groups.

The active intermediates in [Ru(Por*)(CO)(EtOH)]-catalyzed cyclopropanations with alkyl diazoacetates $N_2CHCO_2R$ could be the biscarbene species $[Ru(Por^*)(CHCO_2R)_2]$ or monocarbene species $[Ru(Por^*)(CHCO_2R)(L)]$ (where L is a ligand with considerable trans effect) (Fig. 14), as proposed by Che et al. [20]. This proposal was made on the basis of several lines of evidence. First, the solvent effect in these catalytic cyclopropanations cannot be rationalized simply by the intermediacy of five-coordinate monocarbene species $[Ru(Por^*)(CHCO_2R)]$. Second, neither of the isolated five-coordinate monocarbene species $[Ru(Por^*)(CPh_2)]$ and $[Ru(Por^*)(C(Ph)CO_2CH_2CH{=}CH_2)]$ has been observed to undergo cyclopropanation reaction with an alkene. Although $[Ru(TPP)(C(CO_2Et)_2)]$ can cyclopropanate styrene as mentioned earlier, the reaction occurred at > 100 °C, in contrast to the cyclopropanations catalyzed by [Ru(Por*)(CO)(EtOH)] which can take place at −40 °C. Third, despite the inertness of $[Ru(Por^*)(CPh_2)]$ toward stoichiometric styrene cyclopropanation, this monocarbene complex can catalyze the cyclopropanation of styrene with $N_2CHCO_2Et$ and can sustain > 200 turnovers in the catalytic process, suggesting the functioning of $[Ru(Por^*)(CPh_2)(CHCO_2Et)]$ as an active species in the catalytic cycle (probably, the diphenylcarbene ligand exhibits a large *trans* effect, which increases the reactivity of the $Ru{=}CHCO_2Et$ bond).

Intervention of ruthenium and osmium porphyrin carbene intermediates in the $N_2CHCO_2R$ cyclopropanation of alkenes can also account for the *trans* selectivity generally observed for the ruthenium and osmium porphyrin catalysts. The carbene transfer from

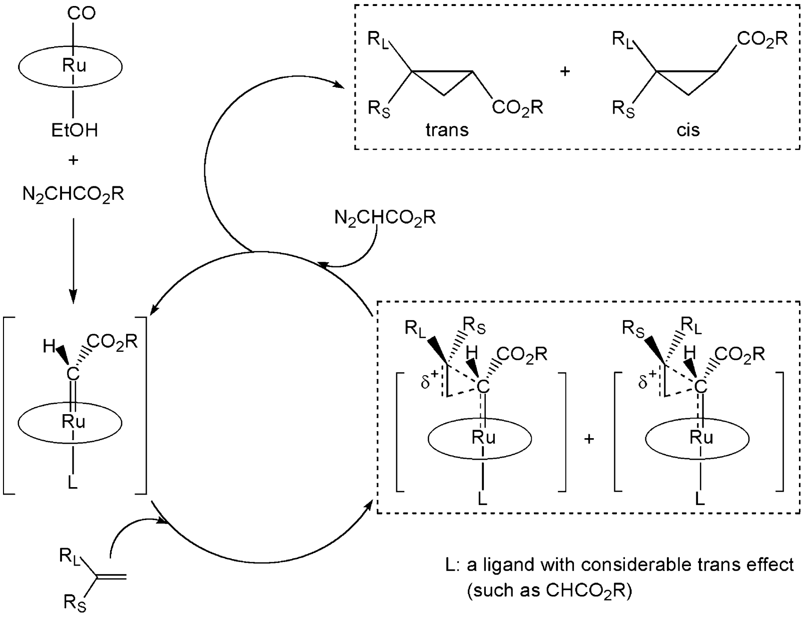


Fig. 14. Proposed catalytic cycle for [Ru(Por*)(CO)(EtOH)]-catalyzed asymmetric cyclopropanation of terminal alkenes with alkyl diazoacetate.

[M(Por)($CHCO_2R$)] (M = Ru, Os) moieties to a terminal alkene $CH_2{=}CR_LR_S$ ($R_L$ and $R_S$ represent large and small groups, respectively) may all proceed via a three-center late transition state (which is depicted, for example, in Fig. 14), as described earlier for the [Ru(TPP)($CHCO_2Et$)] intermediate. The transition state that results in formation of *trans* cyclopropanes should be more stable than that corresponding to *cis* cyclopropanes owing to smaller steric interaction between the alkene and the carbene ligand. This leads to formation of *trans* cyclopropyl esters as the predominant cyclopropanation products.

On the basis of the mechanism shown in Fig. 14, Che et al. have provided a rationalization for the enantiocontrol in the [Ru(Por*)(CO)(EtOH)]-catalyzed cyclopropanation of styrene with $N_2CHCO_2Et$ [20]. They used the structural data of the carbene complex [Ru(Por*)($CPh_2$)] to build a model for the [Ru(Por*)($CHCO_2Et$)] moiety in the proposed ruthenium porphyrin carbene intermediate (Fig. 15), and observed a severe strain between the phenyl group of styrene and the ethano bridge of the adjacent norbornane moiety as styrene approaches the carbene ligand to form the (1*R*,2*R*)-cyclopropyl ester (see Fig. 15b). However, if styrene approaches the carbene ligand to form the (1*S*,2*S*)-cyclopropyl ester, the strain between the styrene phenyl group and the porphyrin norbornane moieties (if any) would be very small (see Fig. 15a). This may account for both the high enantioselectivity and the predominant (1*S*,2*S*) configuration for the *trans* cyclopropyl ester produced in the [Ru(Por*)(CO)(EtOH)]-catalyzed styrene cyclopropanation.

The formation of biscarbene osmium porphyrin [Os(TPFPP)$(CPh_2)_2$] from reaction of either [Os(TPFPP)(CO)] or [Os(TPFPP)($CPh_2$)] with excess $N_2CPh_2$ (reactions (5) and (6) in Fig. 4), the inertness of the monocarbene complex [Os(TPFPP)($CPh_2$)] toward alkene cyclopropanation, and the efficient cyclopropanation of styrene by [Os(TPFPP)$(CPh_2)_2$] both stoichiometrically and catalytically (without induction period) let Che and co-workers propose that the biscarbene osmium porphyrin [Os(TPFPP)$(CPh_2)_2$] serves as an active intermediate in the [Os(TPFPP)(CO)]-catalyzed cyclopropanation of styrene with $N_2CPh_2$ (Fig. 12) [23]. This is the first case in which an isolated and well characterized biscarbene metal complex is likely to function as an active intermediate in metal-catalyzed cyclopropanation of alkenes.

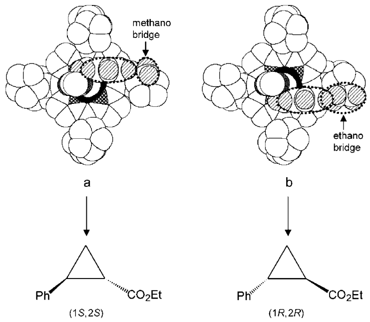


Fig. 15. Top-view space-filling model for the [Ru(Por*)($CHCO_2Et$)] moiety of the proposed active intermediate [Ru(Por*)($CHCO_2Et$)(L)] and the interaction of its carbene ligand with styrene placed: (a) above; and (b) below the carbene plane. Hydrogen atoms are not shown except those in styrene and the indicated methano and ethano bridges.

### 5.2. *Intramolecular cyclopropanation*

By analogy with [Ru(Por*)(CO)(EtOH)]-catalyzed intermolecular cyclopropanations with $N_2CHCO_2R$, Che et al. proposed that the intramolecular cyclopropanations of allylic diazoacetates $N_2CHCO_2CH_2CH{=}CR^cR^t$ catalyzed by [Ru(Por*)(CO)(EtOH)] could occur via the six-coordinate ruthenium porphyrin carbene intermediates [Ru(Por*)(CHX)(L)] ($X = CO_2CH_2CH{=}CR^cR^t$, L = CHX or other ligands with a considerable *trans* effect) [20]. The inertness of closely related five-coordinate carbene complex [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)] toward intramolecular cyclopropanation perhaps provides evidence disfavoring the intermediacy of the five-coordinate intermediate [Ru(Por*)(CHX)].

To rationalize the enantiocontrol in the intramolecular cyclopropanations, they examined the steric interaction of the $R^c$ and $R^t$ groups with the porphyrin ligand in the transition states I–IV depicted in Fig. 16 [20]. The orientation of the H–C–X carbene plane with respect to the Por* ligand in these transition states is established on the basis of the crystal structure of [Ru(Por*)(C(Ph)$CO_2CH_2CH{=}CH_2$)]. When $R^c$ and $R^t$ are small groups such as H or Me, transition states I and II are more stable than III and IV because of the smaller steric interaction between the carbene ligand and the porphyrin ring. However, if $R^c$ is H and $R^t$ is a bulky phenyl group, severe steric interaction occurs between the $R^t$ group and the porphyrin ring in I and II, which renders the two transition states less stable than III and IV. Further inspection of the steric interaction between the $R^c/R^t$ group and the adjacent norbornane moiety A reveals that transition states I and III are more stable than II and IV, respectively (note that the $R^c$ and $R^t$ groups interact with the bulky ethano bridge in II and IV). This accounts for the predominant (1*R*,5*S*) configuration observed for the bicyclic lactone with $R^c = R^t =$ H and the predominant (1*S*,5*R*) configuration for the bicyclic lactones with $R^c = R^t =$ Me and $R^c =$ H, $R^t =$ Ph.

## 6. Summary

Ruthenium and osmium porphyrin carbene complexes have received considerable attention in recent

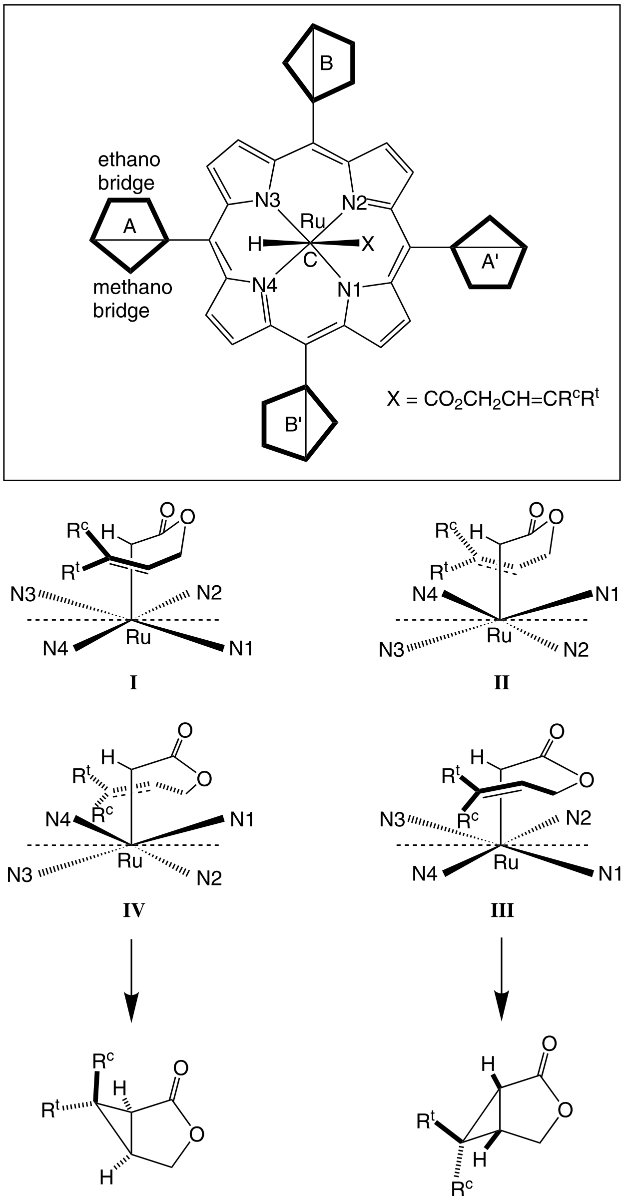


Fig. 16. Schematic structures of the [Ru(Por*)(CHCO$_2$CH$_2$CH=CR$^c$R$^t$)] moiety in the transition states that result in formation of the corresponding bicyclic lactones (only the norbornane moieties at the same side as the carbene group are shown).

years. These interesting classes of organometallic compounds can be readily prepared from the reactions between carbonyl ruthenium/osmium porphyrins and diazo compounds although a few other routes are also available. Their particular importance in the chemistry of metal carbene complexes is reflected by their contributions of the first examples of isolated metal carbene complexes that are active toward catalytic cyclopropanation of alkenes or stoichiometric saturated C–H insertion of unfunctionalized alkenes and the first examples of metalloporphyrin carbene complexes that bear monosubstituted carbene groups CHR, or contain multiple carbene ligands at the axial sites.

Crystallization of monocarbene ruthenium and osmium porphyrins [M(Por)(CRR′)] in solvents containing coordinating molecules L often leads to formation of six-coordinate complexes [M(Por)(CRR′)(L)] with L ligated at the axial sites *trans* to the carbene ligands. However, some of the monocarbene complexes remain five-coordinate even crystallized from solvents containing coordinating molecules. The M=CRR′ bond lengths and the R–C–R′ angles in the five- and six-coordinate monocarbene ruthenium/osmium porphyrins are similar. Interestingly, the structure of *trans*-bis(diphenylcarbene) osmium porphyrin [Os(TPFPP)(CPh$_2$)$_2$] has much longer M=C(carbene) bonds.

The reactivity of ruthenium and osmium porphyrin carbene complexes is currently focused on the osmium ylide formation and carbene transfer to alkenes. These probably stem from the close connection of ruthenium and osmium porphyrin carbene complexes to metal-catalyzed alkene cyclopropanation with diazo compounds. Several ruthenium/osmium porphyrin carbene complexes have been proposed to be the active intermediates in the alkene cyclopropanations catalyzed by ruthenium/osmium porphyrins. The intervention of such ruthenium/osmium carbene intermediates in the catalytic processes accounts well for the observed relative reactivity of substrates and the diastereo- or enantioselectivity of the resultant cyclopropanes.

## Acknowledgements

We acknowledge support from The University of Hong Kong and the Hong Kong Research Grants Council (HKU 7077/01P).

## References

[1] D. Mansuy, M. Lange, J.-C. Chottard, P. Guerin, P. Morliere, D. Brault, M. Rougee, J. Chem. Soc. Chem. Commun. (1977) 648.
[2] H.J. Callot, C. Piechocki, Tetrahedron Lett. 21 (1980) 3489.
[3] D. Mansuy, M. Lange, J.-C. Chottard, J.-F. Bartoli, B. Chevrier, R. Weiss, Angew. Chem. Int. Ed. Engl. 17 (1978) 780.
[4] D. Mansuy, M. Lange, J.-C. Chottard, J. Am. Chem. Soc. 100 (1978) 3214.
[5] D. Mansuy, P. Guerin, J.-C. Chottard, J. Organomet. Chem. 171 (1979) 195.
[6] D. Mansuy, Pure Appl. Chem. 52 (1980) 681.
[7] P. Guerin, J.-P. Battioni, J.-C. Chottard, D. Mansuy, J. Organomet. Chem. 218 (1981) 201.
[8] S. O'Malley, T. Kodadek, Tetrahedron Lett. 32 (1991) 2445.
[9] J.L. Maxwell, K.C. Brown, D.W. Bartley, T. Kodadek, Science 256 (1992) 1544.
[10] J.L. Maxwell, S. O'Malley, K.C. Brown, T. Kodadek, Organometallics 11 (1992) 645.
[11] S. O'Malley, T. Kodadek, Organometallics 11 (1992) 2299.
[12] K.C. Brown, T. Kodadek, J. Am. Chem. Soc. 114 (1992) 8336.
[13] D.W. Bartley, T. Kodadek, J. Am. Chem. Soc. 115 (1993) 1656.

[14] J.P. Collman, P.J. Brothers, L. McElwee-White, E. Rose, L.J. Wright, J. Am. Chem. Soc. 107 (1985) 4570.

[15] L.K. Woo, D.A. Smith, Organometallics 11 (1992) 2344.

[16] D.A. Smith, D.N. Reynolds, L.K. Woo, J. Am. Chem. Soc. 115 (1993) 2511.

[17] E. Galardon, P. Le Maux, G. Simonneaux, Chem. Commun. (1997) 927.

[18] E. Galardon, S. Roué, P. Le Maux, G. Simonneaux, Tetrahedron Lett. 39 (1998) 2333.

[19] W.-C. Lo, C.-M. Che, K.-F. Cheng, T.C.W. Mak, Chem. Commun. (1997) 1205.

[20] C.-M. Che, J.-S. Huang, F.-W. Lee, Y. Li, T.-S. Lai, H.-L. Kwong, P.-F. Teng, W.-S. Lee, W.-C. Lo, S.-M. Peng, Z.-Y. Zhou, J. Am. Chem. Soc. 123 (2001) 4119.

[21] M. Frauenkron, A. Berkessel, Tetrahedron Lett. 38 (1997) 7175.

[22] Z. Gross, N. Galili, L. Simkhovich, Tetrahedron Lett. 40 (1999) 1571.

[23] Y. Li, J.-S. Huang, Z.-Y. Zhou, C.-M. Che, J. Am. Chem. Soc. 123 (2001) 4843.

[24] J.-P. Djukic, V.G. Young, Jr., L.K. Woo, Organometallics 13 (1994) 3995.

[25] J.P. Collman, E. Rose, G.D. Venburg, J. Chem. Soc. Chem. Commun. (1993) 934.

[26] J.P. Collman, P.J. Brothers, L. McElwee-White, E. Rose, J. Am. Chem. Soc. 107 (1985) 6110.

[27] E. Galardon, P. Le Maux, L. Toupet, G. Simonneaux, Organometallics 17 (1998) 565.

[28] F.-W. Lee, Y. Li, C.-M. Che, unpublished results.

[29] D.P. Rillema, J.K. Nagle, L.F. Barringer, Jr., T.J. Meyer, J. Am. Chem. Soc. 103 (1981) 56.

[30] A. Antipas, J.W. Buchler, M. Gouterman, P.D. Smith, J. Am. Chem. Soc. 102 (1980) 198.

[31] J.-P. Djukic, D.A. Smith, V.G. Young, Jr., L.K. Woo, Organometallics 13 (1994) 3020.

[32] M.F. Lappert, P.L. Pye, A.J. Rogers, G.M. McLaughlin, J. Chem. Soc. Dalton Trans. (1981) 701.

[33] M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911.

[34] M.P. Doyle, in: L.S. Hegedus (Ed.), Comprehensive Organometallic Chemistry II, vol. 12, Oxford, Pergamon, 1995, p. 387.

[35] H. Fritschi, U. Leutenegger, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 25 (1986) 1005.

[36] H. Fritschi, U. Leutenegger, A. Pfaltz, Helv. Chim. Acta 71 (1988) 1553.

[37] R.E. Lowenthal, A. Abiko, S. Masamune, Tetrahedron Lett. 31 (1990) 6005.

[38] D.A. Evans, K.A. Woerpel, M.M. Hinman, M.M. Faul, J. Am. Chem. Soc. 113 (1991) 726.

[39] D. Müller, G. Umbricht, B. Weber, A. Pfaltz, Helv. Chim. Acta 74 (1991) 232.

[40] H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, J. Am. Chem. Soc. 116 (1994) 2223.

[41] H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, K. Itoh, Bull. Chem. Soc. Jpn. 68 (1995) 1247.

[42] S.-B. Park, N. Sakata, H. Nishiyama, Chem. Eur. J. 2 (1996) 303.

[43] M.P. Doyle, R.E. Austin, A.S. Bailey, M.P. Dwyer, A.B. Dyatkin, A.V. Kalinin, M.M.Y. Kwan, S. Liras, C.J. Oalmann, R.J. Pieters, M.N. Protopopova, C.E. Raab, D.H.P. Roos, Q.-L. Zhou, S.F. Martin, J. Am. Chem. Soc. 117 (1995) 5763.

[44] E. Galardon, P. Le Maux, G. Simonneaux, Tetrahedron 56 (2000) 615.