J. Am. Chem. Soc. **2001,** *123,* 4843−4844

Isolation and X-ray Crystal Structure of an Unusual Biscarbene Metal Complex and Its Reactivity toward Cyclopropanation and Allylic C−H Insertion of Unfunctionalized Alkenes

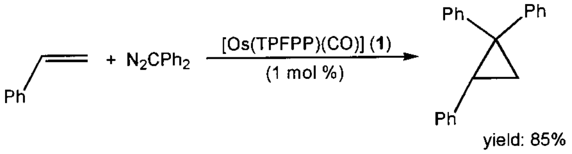
Yan Li,† Jie-Sheng Huang,† Zhong-Yuan Zhou,‡ and
Chi-Ming Che*,†

Department of Chemistry, The University of Hong Kong
Pokfulam Road, Hong Kong
Department of Applied Biology and Chemical Technology
The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong

Received August 28, 2000

The cyclopropanation of alkenes with diazo compounds catalyzed by metal complexes, a carbon analogue of metal-catalyzed epoxidation or aziridination of alkenes, has attracted a myriad of attention.[1] It is widely believed that these cyclopropanation reactions proceed via metal−carbene intermediates, which is supported by the isolation of a few *monocarbene* metal complexes that can undergo stoichiometric cyclopropanation with alkenes.[2] Strikingly, while there are a considerable number of isolated biscarbene metal complexes in the literature,[3−5] along with several tetra- up to hexacarbene species,[6] none of them have been reported to be reactive toward alkene cyclopropanations. In view of the alkene epoxidation/aziridination reactivities observed for dioxo[7]/bisimido[8] ruthenium(VI) porphyrins, we conceive that an alkene cyclopropanation reactivity may be observable for their ruthenium/osmium biscarbene analogues. Herein we describe the isolation and structure characterization of an intriguing *biscarbene* osmium porphyrin. This biscarbene species represents the first structurally characterized *trans*-biscarbene metal complex whose carbene groups are not stabilized by heteroatom(s), has an unprecedentedly long M═C(carbene) bond for such a class of carbene group, allows a *direct* comparison among the structure features of X═M═X (X = CPh_2, NTs, O) functional groups, and can react with unfunctionalized alkenes to form cyclopropanation products. Of particular interest is that this biscarbene species is also reactive toward allylic C−H insertion of unfunctionalized alkenes, constituting the first *isolated* metal−carbene complex exhibiting such reactivity.[9,10]

Several years ago, Woo and co-workers[2a] demonstrated that a simple osmium porphyrin, [Os(TTP)(CO)],[11a] can catalyze the cyclopropanation of alkenes with ethyl diazoacetate (N_2CHCO_2Et), and that an isolated monocarbene complex, [Os(TTP)($CHCO_2Et$)], can undergo stoichiometric cyclopropanation with styrene. In our efforts to extend the "N_2CHCO_2Et + [Os(TTP)(CO)]" system to diphenyldiazomethane (N_2CPh_2) in conjunction with a highly fluorinated osmium porphyrin, [Os(TPFPP)(CO)] (**1**),[11b] we found that complex **1** can catalyze the cyclopropanation of styrene with N_2CPh_2 in dichloromethane at 40 °C to form 1,1,2-triphenylcyclopropane in 85% isolated yield (reaction 1), which represents an efficient metal complex-catalyzed cyclopropanation of an aromatic alkene with diaryldiazomethane.[12] Although treatment of complex **1** with 1 equiv of N_2CPh_2 afforded a monocarbene complex [Os(TPFPP)(CPh_2)] (**2**) in 92% yield, this isolated monocarbene species underwent no stoichiometric cyclopropanation reaction with styrene even at 80 °C under solvent free conditions.



(1)

Interestingly, treatment of complex **2** with excess N_2CPh_2 in dichloromethane gave a *biscarbene* complex, [Os(TPFPP)−(CPh_2)$_2$] (**3**), in 61% isolated yield (reaction 2 in Scheme 1).[13]

---

† The University of Hong Kong.

‡ The Hong Kong Polytechnic University.

(1) For recent reviews, see: (a) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (b) Doyle, M. P.; Protopopova, M. N. *Tetrahedron* **1998**, *54*, 7919. (c) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 387−420. (d) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(2) Selected examples: (a) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511. (b) Park, S.-B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303. (c) Lee, H. M.; Bianchini, C.; Jia, G.; Barbaro, P. *Organometallics* **1999**, *18*, 1961.

(3) For structurally characterized Fischer-type biscarbene complexes whose carbene groups are stabilized by heteroatoms, see: (a) Lappert, M. F.; Pye, P. L.; Rogers, A. J.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 701. (b) Anderson, D. M.; Bristow, G. S.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2843. (c) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (d) Raubenheimer, H. G.; Toerien, J. G.; Kruger, G. J.; Otte, R.; van Zyl, W.; Olivier, P. *J. Organomet. Chem.* **1994**, *466*, 291. (e) Zhang, S.-W.; Kaharu, T.; Pirio, N.; Ishii, R.; Uno, M.; Takahashi, S. *J. Organomet. Chem.* **1995**, *489*, C62. (f) Raubenheimer, H. G.; Olivier, P. J.; Lindeque, L.; Desmet, M.; Hrusak, J.; Kruger, G. J. *J. Organomet. Chem.* **1997**, *544*, 91. (g) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (h) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490. (i) Zhang, S.-W.; Takahashi, S. *Organometallics* **1998**, *17*, 4757. (j) Lee, C. K.; Chen, J. C. C.; Lee, K. M.; Liu, C. W.; Lin, I. J. B. *Chem. Mater.* **1999**, *11*, 1237. (k) Calo, V.; Sole, R. D.; Nacci, A.; Schingaro, E.; Scordari, F. *Eur. J. Org. Chem.* **2000**, 869. (l) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125.

(4) For Schrock-type biscarbene complexes, see: (a) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964. (b) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1048. (c) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930. (d) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802. (e) Diminnie, J. B.; Hall, H. D.; Xue, Z. *Chem. Commun.* **1996**, 2383.

(5) For a bis(diarylcarbene) metalloporphyrin, see: Woo, L. K.; Smith, D. A. *Organometallics* **1992**, *11*, 2344.

(6) (a) Goldberg, S. Z.; Eisenberg, R.; Miller, J. S. *Inorg. Chem.* **1977**, *16*, 1502. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826. (c) Plaia, U.; Stolzenberg, H.; Fehlhammer, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 2171.

(7) (a) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (b) Leung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1989**, *111*, 8812. (c) Ho, C.; Leung, W.-H.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 2933. (d) Lai, T.-S.; Zhang, R.; Cheung, K.-K.; Kwong, H.-L.; Che, C.-M. *Chem. Commun.* **1998**, 1583.

(8) (a) Au, S.-M.; Fung, W.-H.; Cheng, M.-C.; Che, C.-M.; Peng, S.-M. *Chem. Commun.* **1997**, 1655. (b) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120.

(9) For metal-catalyzed carbene group transfer into unactivated saturated C−H bonds that is proposed to involve a metal−carbene intermediate, see: (a) Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssié, P. *J. Chem. Soc., Chem. Commun.* **1981**, 688. (b) Callot, H. J.; Metz, F. *Tetrahedron Lett.* **1982**, *23*, 4321. (c) Davis, H. M. L.; Hansen, T. *J. Am. Chem. Soc.* **1997**, *119*, 9075. (d) Davis, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063.

(10) For intermolecular carbene group transfer from an isolated metal−carbene complex into *unsaturated* C−H bonds, see: (a) Mclain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519. (b) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750. (c) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129.

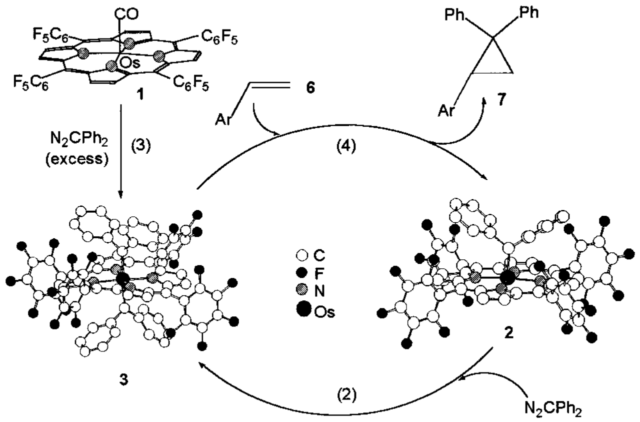
(11) (a) TTP = *meso*-tetrakis(*p*-tolyl)porphyrinato dianion. (b) TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion.

(12) Metal complex-catalyzed cyclopropanations with diaryldiazomethanes are extremely rare and in no such cases are aromatic alkenes (such as styrenes) cyclopropanated in good yields, see: (a) Crumrine, D. S.; Haberkamp, T. J.; Suther, D. J. *J. Org. Chem.* **1975**, *40*, 2274. (b) Doyle, M. P.; Wang, L. C.; Loh, K.-L. *Tetrahedron Lett.* **1984**, *25*, 4087. (c) Pfeiffer, J.; Nieger, M.; Dötz, K. H. *Eur. J. Org. Chem.* **1998**, 1011. (d) Werner, H.; Schneider, M. E.; Bosch, M.; Wolf, J.; Teuben, J. H.; Meetsma, A.; Troyanov, S. I. *Chem. Eur. J.* **2000**, *6*, 3052.

(13) The formation of a biscarbene osmium porphyrin from the reaction of a monocarbene complex with a diazo compound was first observed by Woo and co-workers by ^1H and ^{13}C NMR spectroscopy (see ref 5); however, in their case the biscarbene complex, [Os(TTP)(C(p-C_6H_4Me)$_2$)$_2$], always coexists with the corresponding monocarbene complex and has not been isolated in pure form.

10.1021/ja003184q CCC: $20.00

Scheme 1



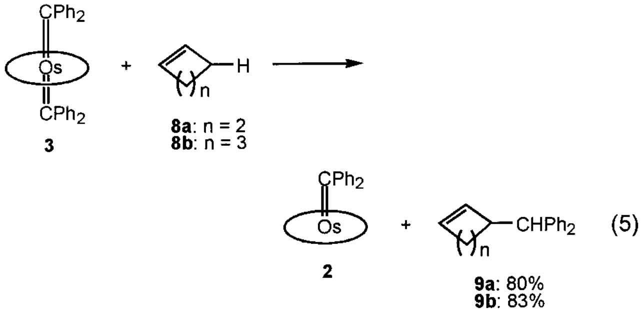
Complex **3** can also be prepared in a similar yield from a direct reaction of complex **1** with excess N_2CPh_2 (reaction 3 in Scheme 1). The ^{13}C NMR spectra of **2** and **3** show a low-field signal at 273.60 and 313.79 ppm, respectively, which are typical for metal−carbene complexes.[5]

Both complexes **2** and **3** have been characterized by X-ray structure determinations. The structure of the biscarbene complex **3** shows several unusual features. First, compared with the Os═C(carbene) bond lengths in monocarbene complexes **2** (1.870(2) Å) and [Os(TTP)(C(*p*-$C_6H_4Me)_2$)] (1.856(8) Å),[14] the corresponding bond lengths in **3** (2.035(2) and 2.027(3) Å) are rather long.[15] Such a large difference in the Os−C(carbene) distance between mono- and biscarbene complexes **2** and **3** can be attributed to the trans effect of the CPh_2 group and could account for the dramatic difference in their reactivity (see below). Second, the $Ph_2C{=}Os{=}CPh_2$ moiety in **3** adopts a roughly perpendicular arrangement of the two carbene groups (similar to allenes $R_2C{=}C{=}CR_2$), unlike the parallel arrangement of the heteroatom-stabilized carbene groups in an octahedral *trans*-biscarbene molybdenum complex.[3a] Third, the porphyrin ring in **3** exhibits a large ruffling distortion with a mean deviation of 0.197 Å from its least-squares plane, in contrast to the basically planar porphyrin ring in the monocarbene complex **2** with a mean deviation of 0.0382 Å.

The formation of **3** from reaction of **1** with excess N_2CPh_2 formally resembles the reaction between **1** and excess PhI═NTs or *m*-CPBA to form [Os(TPFPP)$(NTs)_2$] (**4**) or [Os(TPFPP)O_2] (**5**), respectively, both of which have been isolated and characterized by X-ray structural determinations (Os═NTs 1.803(3), 1.799(3) Å; Os═O 1.741(2) Å). *Direct* comparison of the spectral and structural features among the biscarbene, bisimido, and dioxo metal complexes (Table S1) reveals a substantially smaller H_β chemical shift[16] and a much longer M−L axial bond for the biscarbene complex **3** than for the bisimido and dioxo complexes **4** and **5**.

Treatment of **3** with styrene and its derivatives **6** at 80 °C afforded the corresponding cyclopropanes **7** in 70−94% yields (reaction 4 in Scheme 1 and Table S2), accompanied by formation of the monocarbene complex **2**. In contrast, neither **4** nor **5** was found to undergo imido or oxo group transfer reaction with an alkene. Reaction 4 also occurred in dichloromethane at 40 °C but proceeded more slowly under these conditions. A striking feature of the cyclopropanation by **3** lies in the high yield achieved for *trans*-β-methylstyrene (92%), which has not been reported to be a good substrate for the cyclopropanations mediated by other metalloporphyrins.[2a,17] Competitive cyclopropanation of styrene and para-substituted styrenes *p*-X-$C_6H_4CH{=}CH_2$ (X = MeO, Me, Cl, CF_3) by **3** revealed that the cyclopropanation process is promoted by the electron-donating but retarded by the electron-withdrawing substituents, and the $\log(k_X/k_H)$ vs σ^+ plot exhibits a linearity with $\rho^+ = -1.28 \pm 0.08$ and $R = 0.99$ (see Figure S1).

Remarkably, the reaction between complex **3** and cyclopentene (**8a**) or cyclohexene (**8b**) resulted in transfer of the carbene group selectively into the allylic C−H bonds, affording respective diphenylmethyl-substituted cyclic alkenes (**9**) in ~80% yields (reaction 5).



It should be noted that reactions 4 and 5 are unlikely to proceed via free CPh_2 species in solution. Upon preparation of [Os(TPFPP)$(CPh_2\text{-}d_{10})_2$] (**3**-d_{20}) from **1** and excess N_2CPh_2-d_{10}, we conducted a crossover experiment, which showed that no crossover product, [Os(TPFPP)$(CPh_2)(CPh_2\text{-}d_{10})$], is formed in an equimolar mixture of **3** and **3**-d_{20} in dichloromethane at 40 °C.

The present work provides new insight into the intermediates in metal-catalyzed cyclopropanation of alkenes. The inertness of **2** toward stoichiometric styrene cyclopropanation and the observation of reactions 2−4 (Scheme 1) suggest that the *biscarbene* species **3** acts as an active intermediate in reaction 1. This is further supported by an efficient cyclopropanation of styrene with N_2CPh_2 in the presence of a catalytic amount of **3**, which afforded the cyclopropane product in 63% isolated yield without an induction period under the same conditions as for catalyst **1**.[18]

Acknowledgment. This work was supported by The University of Hong Kong (the Generic Drug Research Program), the Hong Kong University Foundation, and the Hong Kong Research Grants Council (HKU 501/96P).

Supporting Information Available: Experimental details (including the spectral data of all the new compounds reported in this work), Tables S1 and S2, Figure S1, and the X-ray structure determinations of complexes **2**·2MeOH, **3**·$2H_2O$·CH_2Cl_2, **4**·CH_2Cl_2, and **5**·MeOH (including the ORTEP drawings, crystal data and structure refinements, tables of final coordinates, bond lengths, bond angles, and anisotropic displacement parameters) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003184Q

---

[14] Djukic, J.-P.; Smith, D. A.; Young, V. G., Jr.; Woo, L. K. *Organometallics* **1994**, *13*, 3020.

[15] Although the Os−C(CPh_2) distance in **3** is similar to an Os−C(alkyl) distance (compare with the Os−C(CH_2SiMe_3) distance of 2.070(6) Å in *cis*-[Os$(CHBu^t)_2(CH_2SiMe_3)_2$] reported in ref 4d), it is unlikely that the CPh_2 units in **3** belong to $CHPh_2$ groups in view of the ^{13}C NMR spectral feature of **3** and the virtually planar arrangement of both the Os−CPh_2 moieties in **3** (see Table S1).

[16] The chemical shift for the pyrrole protons of the porphyrin macrocycle in the ^1H NMR spectrum (δ = 8.26, 9.06, and 9.22 for the diamagnetic species **3**, **4**, and **5**, respectively). Note that for a diamagnetic metalloporphyrin, the H_β chemical shift usually increases with the oxidation state of the metal ion, see: Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 198.

[17] Other representative examples: (a) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489. (b) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645. (c) Wolf, J. R.; Hamaker, C. G.; Djukic, J.-P.; Kodadek, T.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 9194. (d) Galardon, E.; Le Maux, P.; Simonneaux, G. *Chem. Commun.* **1997**, 927. (e) Lo, W.-C.; Che, C.-M.; Cheng, K.-F.; Mak, T. C. W. *Chem. Commun.* **1997**, 1205. (f) Frauenkron, M.; Berkessel, A. *Tetrahedron Lett.* **1997**, *38*, 7175.

[18] The lower yield obtained for the cyclopropanation catalyzed by **3** than by **1** (63 vs 85%) may indicate that **3** is the prevailing but not the sole active intermediate in the latter system.