Synthesis, Crystal Structure, and Reactivity of (5,10,15,20-Tetraphenylporphyrinato)ruthenium(II) (Diethoxycarbonyl)carbene Methanol

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The new (porphyrin)ruthenium(II) carbene complex **1** has been prepared by treating (TPP)-Ru(CO)[EtOH] with excess diethyl diazomalonate. The good stability of this complex allowed us to determine its structure by single-crystal X-ray diffraction. The reactivity of **1** toward various axial ligands (CO, pyridine, triphenylphosphine) is also discussed, as well as its ability, from ethyl diazoacetate, to catalyze the coupling formation of olefins and the cyclopropanation of styrene.

Introduction

Recent growth in the area of transition-metal porphyrin chemistry has, in part, been driven by the increased interest associated with metal-catalyzed cyclopropanation. Examples involving rhodium,[1,2] osmium,[3] and iron[4] porphyrins as catalysts have been previously reported. Rhodium catalysts produce synthetically useful excesses of cis cyclopropyl esters using ethyl diazoacetate as the carbene source, whereas under the same conditions, osmium and iron catalysts mainly provide the trans product. Catalytic production of olefins from ethyl diazoacetate has been recently reported with osmium[5] and ruthenium[6] porphyrins. Despite the periodic relationship of ruthenium to iron and osmium and the syntheses of different carbene complexes of ruthenium porphyrins, nicely developed by Collman et *al.*,[6,7] it has only been very recently that cyclopropanation and ethyl diazoacetate insertion into heteroatom bond reactions have been observed using ruthenium porphyrins as catalysts.[8] Recently, a set of stable chiral ruthenium bis(oxazolinyl)pyridine carbene complexes were also isolated and studied by Nishiyama and co-workers.[9] Catalytic asymmetric cyclopropanation of styrene with aryl diazoacetates with these complexes resulted in formation of *anti* 2-phenylcyclopropane carboxylates with high enantioselectivity.[9b] As part of our continuing effort to develop ruthenium porphyrin chemistry, we report now the synthesis, crystal structure, and reactivity of an air-stable (5,10,-15,20-tetraphenylporphyrinato)ruthenium (diethoxycarbonyl)carbene complex. To our knowledge, this is the first (porphyrin)ruthenium(II) carbene complex that has been characterized by single-crystal X-ray diffraction analysis.

Results and Discussion

Synthesis. Four different methods have been developed for the preparation of (porphyrin)ruthenium carbene complexes: (i) insertion of $Ru_3(CO)_{12}$ into the C−N bonds of N,N′-bridged porphyrins,[10] (ii) direct cleavage[7a] of ruthenium porphyrin dimers[11,12] with diazo derivatives, (iii) treatment of zerovalent ruthenium porphyrin dianions with geminal dihalides,[7b] and (iv) direct addition of diazo derivatives[6] to monomeric 14-electron ruthenium porphyrins.[13] All these syntheses are lengthy and quite tedious. We recently discovered a simple method to ligate carbenes directly onto ruthenium

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(1) (a) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489. (b) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 311. (c) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365. (d) Callot, H. J.; Metz, F. *Nouv. J. Chim.* **1985**, *9*, 167.

(2) (a) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645. (b) O'Malley, S.; Kodadek, T. *Organometallics* **1992**, *11*, 2299.

(3) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511.

(4) Wolf, J. R.; Hamaker, C. G.; Djukic, J. P.; Kodadek, T.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 9194.

(5) Woo, L. K.; Smith, D. A. *Organometallics* **1992**, *11*, 2344.

(6) Collman, J. P.; Rose, E.; Venburg, G. D. *J. Chem. Soc., Chem. Commun.* **1993**, 934.

(7) (a) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570. (b) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110. (c) Collman, J. P.; McElwee- White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332. (d) Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209.

(8) (a) Galardon, E.; Le Maux, P.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1997**, 927. (b) Lo, W. C.; Che, C. M.; Cheng, K. F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1205. (c) Frauenkron, M.; Berkessel, A. *Tetrahedron Lett.* **1997**, *38*, 7175. (d) Galardon, E.; Le Maux, P.; Simonneaux, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2455.

(9) (a) Park, S. B.; Nishiyama, H.; Itoh, Y.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1315. (b) Park, S. B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303. (c) Nishiyama, H.; Aoki, K.; Itoh, H.; Iwamura, T.; Sakata, N.; Kurihara, O.; Motoyama, Y. *Chem. Lett.* **1996**, 1071.

(10) Chan, Y.; W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888.

(11) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.

(12) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 7030.

(13) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137.

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Table 1. ^{1}H NMR Data for the (TPP)Ru[:C(CO$_2$Et)$_2$](L) Complexes (δ, ppm)

complex	L	$H_{pyrrole}$	H_o	$H_{o'}$	$H_{m,p}$	CH_2	CH_3
1		8.56	8.13		7.69	2.63	0.36
2	7.12 (m, 9H), 6.33 (m, 6H)	8.48	8.12	7.94	7.67	2.57	0.32
3	6.71 (br, 5H)	8.44	8.18	8.00	7.65	2.59	0.35

porphyrins, using carbonyl complexes as starting materials.[8a,d]

Reaction of the carbonyl compound (TPP)Ru(CO)[EtOH][14] with excess diethyl diazomalonate[15] in refluxing chloroform results in the displacement of the CO ligand and generation of the dark brown carbene derivative **1** in 64% isolated yield (eq 1). The (TPP)Ru[:C(CO$_2$Et)$_2$][MeOH] compound is air-stable in the solid state[16] and soluble in common polar organic solvents. This new product has been characterized by conventional spectroscopic techniques. In particular, its IR spectrum as a KBr pellet reveals the presence of a single absorption at 1702 cm^{-1}, attributed to the CO$_2$Et groups, and the absence of the CO absorption due to the axial ligand. The ^{13}C NMR spectrum shows a typical low-field signal[9] for the carbene carbon at 271.35 ppm, and the ^{1}H NMR spectrum reveals a quadruplet and a triplet for the carbene fragment at 2.63 ppm (CH$_2$) and 0.36 ppm (CH$_3$) (Table 1). These two resonances are shifted upfield relative to those of the free diethyl diazomalonate, 4.27 and 1.29 ppm respectively, because of the porphyrin ring current effect. In UV–vis spectroscopy, the coordination of the carbene species slightly modifies the absorption spectrum of the starting carbonyl complex: the Soret band undergoes a 4 nm blue shift when the Q-band becomes broad and undergoes a 4 nm red shift. All these spectroscopic properties are in agreement with previous data for (porphyrin)ruthenium carbene complexes.[6,7a]

$$\text{(TPP)Ru(CO)[EtOH]} + N_2{=}C(CO_2Et)_2 \xrightarrow[\text{MeOH}]{\text{CHCl}_3} \underset{\mathbf{1}}{\text{(TPP)Ru[:C(CO}_2\text{Et)}_2\text{][MeOH]}} + CO + N_2 + EtOH \qquad (1)$$

This method was found effective for other diazo derivatives (RR′CN$_2$: R = H, CH$_3$, R′ = CO$_2$Et).[8a,d] It represents a useful substitution of the previous methods which all, except for one,[10] used photochemical carbonyl ejection and formation of either a ruthenium porphyrin dimer with unencumbered porphyrins or a 14-electron bare (5,10,15,20-tetramesitylporphyrinato)ruthenium complex.[13] These last two derivatives are highly oxygen sensitive, whereas (porphyrin)ruthenium carbonyl derivatives are easily prepared and are air-stable.

Table 2. Crystallographic Data for 1

empirical formula	$C_{52}H_{42}N_4O_5Ru{\cdot}H_2O$
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	18.502(6)
b (Å)	13.552(5)
c (Å)	18.494(6)
β (deg)	90.85(3)
V (Å$^{3)}$	4637(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.312
F(000)	1900
μ(Mo Kα) (cm^{-1})	3.81
T (K)	294
cryst size (mm)	0.22 × 0.31 × 0.38
radiation	Mo Kα
max 2θ (deg)	50
scan	$\omega/2\theta = 1$
t_{max} (for one measmt), s	60
variance of stds	0.2
range of hkl	0−21; 0−15; −21 to +21
no. of rflns measd	7874
no. of rflns obsd ($I > \sigma(I)$)	3611 (4σ)
R_{int} (from merging equiv rflns)	0.025
R(isotropic)	0.105
R(anisotropic)	0.073
difference Fourier	0.72−0.20
N(obs)/N(var)	3611/563
final R	0.057
R_w[a]	0.051
S_w	3.21
max residual (e Å^{-3}), Δ/σ	0.72, 0.11

[a] $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^{\,2})^2]^{-1/2}$.

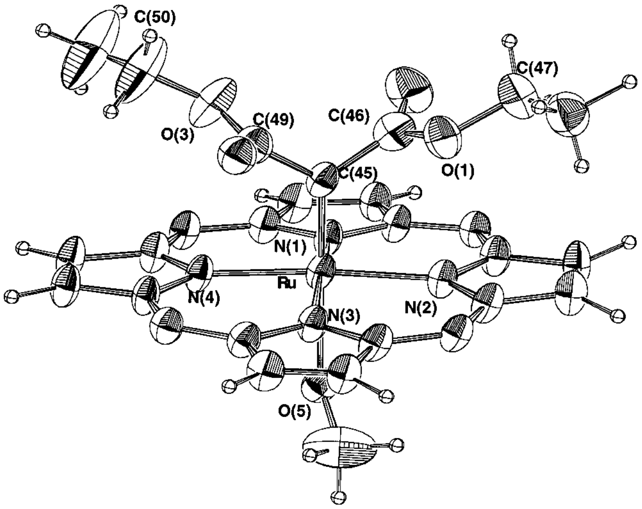

Figure 1. Molecular structure and atom labeling of **1** (phenyl rings are omitted for clarity).

Crystal and Molecular Structure of (TPP)Ru[:C(CO$_2$Et)$_2$][CH$_3$OH]. The diethoxycarbene complex **1** forms as purple crystals in the monoclinic space group $P2_1/n$ with four molecules per unit cell. Crystallographic data for the structure determination are given in Table 2. Figure 1 illustrates the molecular structure and atom labeling. Selected distances and bond angles are given in Table 3. As indicated by the structure, the

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(14) TPP is 5,10,15,20-tetraphenylporphyrin dianion. (TPP)Ru(CO)[EtOH] is a six-coordinate complex containing a weakly bonded axial ligand (L = EtOH); such a ligand is easily removed: Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141.

(15) *Caution*! The potentially explosive nature of diazo compounds should be kept in mind, particularly during distillation: Rosenberg, M.; Yates, P. *Tetrahedron Lett.* **1964**, *33*, 2285.

(16) Although many studies of (porphyrin)iron carbene complexes have been conducted, they are made difficult by the extreme ease with which iron(II) is oxidized. See for example: (a) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781. (b) Mansuy, D.; Guerin, P.; Chottard, J. C. *J. Organomet. Chem.* **1979**, *171*, 195. (c) Guerin, P.; Battioni, J. P.; Chottard, J. C.; Mansuy, D. *J. Organomet. Chem.* **1981**, *218*, 201. (d) Artaud, I.; Gregoire, N.; Battioni, J. P.; Dupré, D.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8714. (e) Artaud, I.; Gregoire, N.; Leduc, P.; Mansuy, D. *J. Am. Chem. Soc.* **1990**, *112*, 6899.

Table 3. Selected Bond Distances (Å) and Angle (deg) for 1

Ru−N(1)	2.045(5)	C(45)−C(46)	1.49(1)
Ru−N(2)	2.045(5)	C(45)−C(49)	1.51(1)
Ru−N(3)	2.048(6)	C(46)−O(1)	1.33(1)
Ru−N(4)	2.047(6)	C(49)−O(3)	1.31(1)
Ru−C(45)	1.829(9)	O(1)−C(47)	1.47(1)
Ru−O(5)	2.293(6)	O(3)−C(50)	1.45(1)
C(45)−Ru-O(5)		178.5(3)	

carbene complex exists as a 6-coordinate compound, with a methanol molecule as axial ligand. As expected for such a complex, the porphyrin ligand is nearly planar. However, the ruthenium atom is slightly out of the mean porphyrin plane, 0.12 Å toward the carbene ligand. A similar situation has previously been observed with a (porphyrin)osmium(II) carbene complex[17] and with a porphyrin rhodium(III) carbene complex.[18] The Ru−N distances of 2.045(5)−2.048(6) Å all fall within the range previously reported for diamagnetic (TPP)Ru(CO)[EtOH].[14] The geometry of the coordination sphere is close to an ideal octahedral geometry. Bond angles at ruthenium are in the range 89.1(2)−90.5(2)° for cis angles and 169.5(3)−174.5(3)° for trans angles. The O−Ru−C(carbene) angle is 178.5(3)°. The carbene fragment is slightly distorted, since the angle formed by C(42)−C(45)−C(46) is 112.2(7)°. Such a value, which is significantly smaller than the 120° angle for ideal sp^2 hybridization, has been previously reported for a (porphyrin)osmium carbene complex: (5,10,15,20-tetra-*p*-tolylporphyrinato)osmium (trimethylsilyl)methylidene.[17] Steric interactions between the two ethoxy groups of the carbene fragment and the phenyl groups of the porphyrin may explain this result. However, a similar angular value was also found for the bis(methoxycarbonyl)carbene ligand in the molecular structure of (pybox)Ru(Cl)$_2$[:C(CO$_2$Me)$_2$][9c] (pybox = 2,6-bis[(4*S*)-isopropyloxazolin-2-yl]pyridine), which is a nonporphyrin complex.

The Ru−C distance of 1.829(9) Å is slightly shorter than ruthenium−carbon double bonds reported for other molecular structures of ruthenium carbene complexes. For examples, the ruthenium−carbon distances in (pybox)Ru(Cl)$_2$[:C(CO$_2$Me)$_2$],[9c] Ru(Cl)$_2$(PPh$_3$)$_2$[:CH−CH=CPh$_2$],[19] and CpRu(I)(CO)[:C(OEt)Ph][20] are 1.880(7), 1.887(7), and 1.997(5) Å, respectively. For comparison, the M=C distances of the rare (porphyrin)metal carbene complexes which have been characterized by single-crystal X-ray diffraction analysis are 1.83(3) Å in (TPP)Fe[:C(Cl)$_2$][H$_2$O],[16a] 1.865(5) Å in (TTP)Os[:C(C$_6$H$_4$-*p*-CH$_3$)$_2$][THF],[17] 1.79(2) Å in (TTP)Os[:C(H)(SiMe$_3$)][THF],[17] and 2.030(11) Å in (TPP)Rh(PhCH$_2$NC)[:C(NHCH$_2$Ph)$_2$]PF$_6$.[18] The Ru^{II}−O distance of 2.293(6) Å is slightly longer than the corresponding Ru^{II}−O distance of 2.21(2) Å found in the similar complex (TPP)Ru(CO)[EtOH].[14]

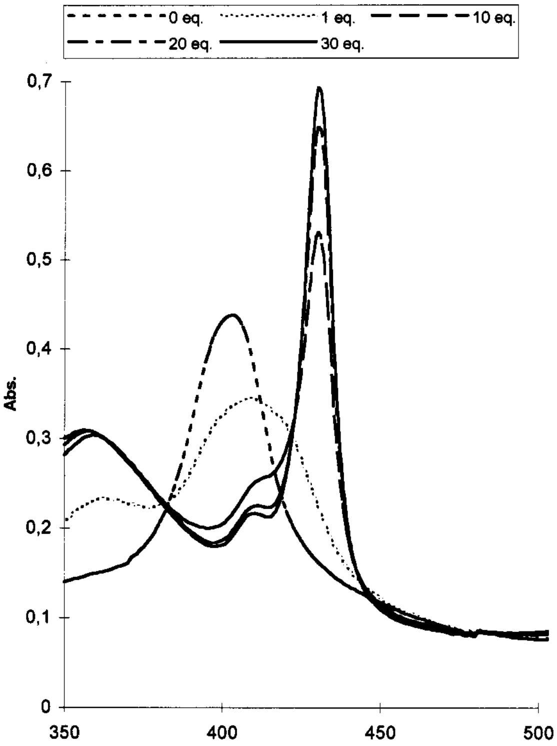

Figure 2. Titration curves of a solution of **1** in CH$_2$Cl$_2$ (2.14 mM) with a solution of PPh$_3$ in dichloromethane (1.25 M).

Ligand-Exchange Reactions. Since the catalytic role of metalloporphyrins is certainly dependent on the chemistry of the axial ligands, we decided to investigate the reaction between **1** and various axial ligands (trans effect). As in the case with the carbonyl complex,[14,21] the carbene complex of ruthenium porphyrin in solution shows a large affinity for a second axial ligand and the magnitude of this effect is dependent on the nature of the ligand. Nevertheless, this reaction is sufficiently slow to be monitored by UV−vis spectroscopy.

The two titration curves with triphenylphosphine and pyridine are shown in Figures 2 and 3, respectively. Modification of the wavelength of the Soret band reveals in both cases the presence of an intermediate (λ_{max} 409 nm for **2** and λ_{max} 410 nm for **3**) which appears after addition of 1 equiv of ligand. These intermediates were identified by ^{1}H NMR spectroscopy as the mixed base−carbene complex **2** (base = triphenylphosphine) and **3** (base = pyridine). For example, the spectrum of complex **2** shows only one signal in the region of the β-pyrrole proton (δ 8.48 ppm) and upfield resonances corresponding to the carbene moiety (δ 2.57 and 0.32 ppm) with broad signals corresponding to the coordinated base (δ 7.12 and 6.33 ppm) (Table 1). Moreover, the differentiation of the H$_o$ signals (Δ = 0.18 ppm) is in agreement with two different ligated groups. Addition of a large excess of base results in the formation of the symmetric bis-ligated derivative, as identified by UV−vis[22,24] and ^{1}H NMR.[22,23] As shown in Figures 2

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(17) Djukic, J. P.; Smith, D. A.; Young, V. G., Jr.; Woo, L. K. *Organometallics* **1994**, *13*, 3020.

(18) Boschi, T.; Licoccia, S.; Paolesse, R.; Tagliatesta, P.; Pelizzi, G.; Vitali, F. *Organometallics* **1989**, *8*, 330.

(19) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

(20) Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349.

(21) (a) Tutsui, M.; Ostfeld, D.; Hoffman, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 1820. (b) Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1971**, *1*, 57. (c) Eaton, S. S.; Eaton, G. R.; Holm, R. H. *J. Organomet. Chem.* **1972**, *39*, 179. (d) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1977**, *16*, 72.

(22) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B.; Leung, T. W.; Rettig, S.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.

(23) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015.

(24) Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5939.

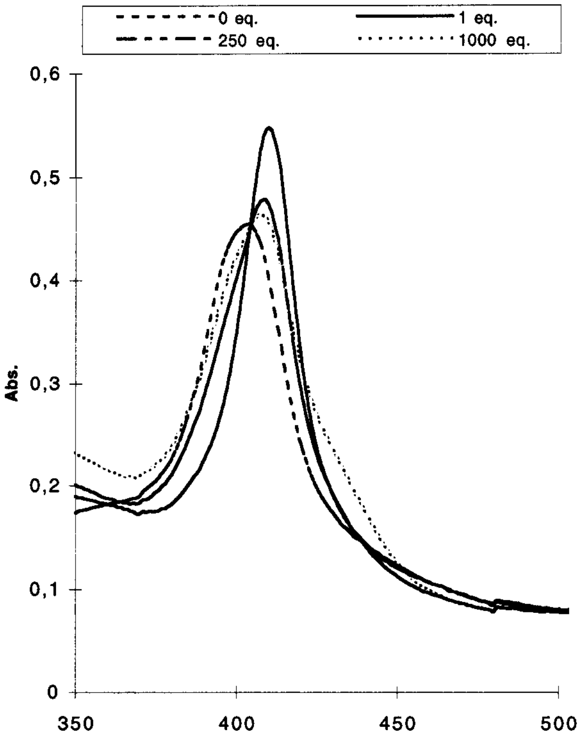


Figure 3. Titration curves of a solution of **1** in CH_2Cl_2 (2.14 mM) with a solution of pyridine in dichloromethane (1.25 M).

and 3, the destabilization of the Ru=C bond is higher with triphenylphosphine than with pyridine: the carbene ligand is completely displaced after addition of 30 equiv of phosphine, while more than 1000 equiv of pyridine is required for the carbene exchange under similar experimental conditions. Thus, coordination of basic ligands, such as triphenylphosphine and pyridine, destabilizes the ruthenium–carbene bond and leads to the axially symmetric bis-ligated complex. Similar behavior has already been reported by Mansuy and coworkers with (porphyrin)iron carbene complexes.[16c]

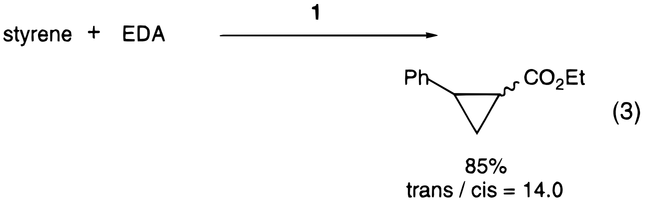
We also investigated the interaction between **1** and CO. During slow bubbling of carbon monoxide in a solution of **1** in dichloromethane, the reaction mixture turned red, and a precipitate appeared. Its IR spectrum revealed, after stirring of the solution under argon and precipitation of the complex, the presence of a carbonyl band at 1943 cm^{-1}, which is in the range for typical ruthenium carbonyl compounds.[24,25] Absence of the ester band indicates the decoordination of the carbene moiety. Formation of (TPP)Ru(CO) has been confirmed by ^1H NMR spectroscopy. No evidence for a mixed carbonyl–carbene derivative has been found by monitoring the reaction by IR. In all the substitution reactions, free methanol is detected, as well as some unidentified organic products resulting from the carbene ligand removal.

Carbene Transfer Reaction, Catalytic Formation of Olefins, and Cyclopropanation. The postulate of possible metallocarbenes as active intermediates in cyclopropanation reactions[26] together with our recent results in catalysis[8a,d] prompted us to investigate the reactivity of **1** toward ethyl diazoacetate (EDA) and styrene.

First, we examined the possibility of the stoichiometric carbene transfer reaction from **1** to styrene, although the complex is quite stable. This transfer was successful by addition of a 30-fold excess of olefin to **1** in refluxing toluene, giving the corresponding cyclopropane[27] in 66% yield. Analysis of the ruthenium complex mixture at the end of the reaction showed the presence of (TPP)Ru(CO) (IR: ν 1954 cm^{-1}, 15%) together with unidentified products. Such decarbonylation of acid derivatives by metalloporphyrin complexes is not unusual and has already been observed.[21b,28]

Then we investigated the potential of **1** in the catalyzed formation of olefins and cyclopropanation of styrene by EDA. When a dichloromethane solution of **1** is treated with excess ethyl diazoacetate, rapid evolution of gas is observed and high yields (>95%) of diethyl maleate and fumarate are obtained in the ratio 13.8/1 (eq 2). During this catalytic reaction, **1** is partially transformed (ca. 10%) to the new complex **4**. Its ^1H NMR spectrum displays a singlet at 13.03 ppm, which allowed us to characterize this product as (TPP)Ru[:C(CO_2Et)(H)] by comparison with an authentic sample prepared from (TPP)Ru(CO)[EtOH] and N_2=CH(CO_2Et). However, in contrast to the catalytic formation of olefins with (porphyrin)osmium carbene complexes,[5] where a bis(carbene) derivative was proposed to be the intermediate, no evidence of such species could be obtained with **1** as catalyst. The catalytic reaction of styrene and EDA was also carried out to give in 85% yield the corresponding ethyl 2-phenylcyclopropane-1-carboxylate (eq 3), with trans/cis selectivity (14.0/1) similar to that observed when (TPP)Ru(CO)[EtOH] was used as a catalyst.[8a] The final metal products are essentially the original carbene complex and traces of **4**. Consequently, all these catalytic reactions seem to involve a common intermediate, which may be the 14-electron bare ruthenium porphyrin complex [(TPP)Ru], but much work is needed to address the mechanistic issues of these ruthenium-catalyzed processes.

$$\mathrm{EDA} \xrightarrow{\mathbf{1}} \mathrm{EtO_2CH{=}CHCO_2Et} \quad \underset{\text{cis / trans = 13.8}}{> 95\%} \qquad (2)$$



Experimental Section

Materials. Solvents were distilled from phosphorus pentoxide (dichloromethane, chloroform), sodium (pentane), or sodium benzophenone (toluene). All chemicals were obtained from Acros Organics and used as received. All manipulations were carried out under an argon atmosphere.

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[25] Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 235.

[26] Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919 and references therein.

[27] Fraser, W.; Suckling, C. J.; Wood, H. C. S. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3137.

[28] Belani, R.; James, B. R.; Dolphin, D.; Rettig, S. J. *Can. J. Chem.* **1988**, *66*, 2072.

Physical Measurements. UV−visible spectra were recorded on an Uvikon 941 spectrophotometer in dichloromethane. Infrared spectra were obtained in KBr or CH_2Cl_2 on a Nicolet 205 FT-IR spectrophotometer. NMR spectra were recorded in $CDCl_3$ on 200 DPX ((200 MHz (^1H), 50 MHz (^{13}C)) and referenced against the residual proton resonance of the deuterated solvent. FAB mass spectrometry was performed by the Centre Regional de Mesures Physiques de l'Ouest (CRMPO) at Rennes, France, on a ZabSpec multisources spectrometer.

Structure Determination of 1 by Single-Crystal X-ray Diffraction. The sample (0.22 × 0.31 × 0.38 mm) was studied on an ENRAF-Nonius automatic diffractometer CAD4 with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max} = 50°$; scan $\omega/2\theta = 1$; $t_{max} = 60$ s; *hkl* range *h* 0−21, *k* 0−15, *l* −21 to +21; intensity controls without appreciable decay (0.2%)) gives 7874 reflections, of which 3611 are independent ($R_{int} = 0.025$) with $I > 4\sigma(I)$. After Lorentz and polarization corrections, the structure was solved with direct methods,[29] which revealed many non-hydrogen atoms of the structure. The remaining atoms (and a water molecule) were found after several scale factor and Fourier difference calculations. After isotropic ($R = 0.105$) and then anisotropic refinement ($R = 0.073$), many hydrogen atoms were found with a difference Fourier calculation (between 0.72 and 0.20 e Å^{-3}), the remaining ones being set in theoretical positions. The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Ru, N, and C atoms, x, y, z fixed for hydrogen atoms; 563 variables and 3611 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting $R = 0.057$, $R_w = 0.051$, and $S_w = 3.21$ (residual $\Delta\rho \leq 0.72$ e Å^{-3}). Atomic scattering factors were taken from ref 30. All the calculations were performed on a Silicon Graphics Indy Computer with the MOLEN package for refinement and Ortep calculations.[31]

Synthesis of (TPP)Ru[:C(CO_2Et)$_2$] (1). In a 250 mL three-neck round-bottomed flask fitted with a septum, reflux condenser, and argon inlet port were added 40 mL of distilled $CHCl_3$ and 800 mg (1.08 mmol) of (TPP)Ru(CO)[EtOH]. The solution was gently refluxed; then 300 mg (1.62 mmol) of diethyl diazomalonate was added via syringe. The reaction was monitored by UV−vis spectroscopy. After about 30 min, the solvent was removed and the dark brown complex was washed with pentane and a small amount of methanol. The final product (622 mg, 64%) was greater than 95% as evidenced by NMR spectroscopy. Microcrystals suitable for X-ray structure analysis were obtained by recrystallization from methanol. ^1H NMR: δ 8.56 (s, 8H); 8.13 (m, 8H); 7.69 (m, 12H); 2.63 (q, 4H); 0.36 (t, 6H). ^{13}C NMR: δ 271.36; 173.77; 144.78; 142.84; 134.82; 133.99; 132.01; 127.92; 126.96; 127.08; 122.98; 59.28; 14.02. UV−vis: (λ_{abs}, nm (ϵ, M^{-1} cm^{-1})): 406 (126 000); 531 (13 000). FAB mass (m/z): calcd for $C_{51}H_{38}N_4O_4Ru$ ($M^+ - MeOH$): 872.1951, found 872.1924.

Ligand-Exchange Reaction of 1 with CO. Carbon monoxide was bubbled through a solution of 10 mg (10.7 μmol) of **1** in 5 mL of dichloromethane for 2 h. The reaction mixture was then stirred under a CO atmosphere for 18 h, before isolating the product identified as (TPP)Ru(CO)[EtOH][14] (89% yield).

Carbene Transfer from 1 to Styrene. An 80 mg (86 μmol) amount of **1** and 296 μL (258 μmol) of styrene in 40 mL of toluene were refluxed for 48 h. The solvent was then removed and the mixture analyzed by GC and ^1H NMR. Diethyl 2-phenylcyclopropane-1,1-dicarboxylate was analyzed by comparison with literature data (66% yield).[27]

Catalytic Formation of Olefins from EDA. A 167 μL portion of ethyl diazoacetate (1.607 mmol) was added slowly (ca. 1 h) via syringe to a well-stirred solution of 10 mg (10.7 μmol) of **1** in dichloromethane. After it was stirred at room temperature for 15 min, the reaction mixture was analyzed by GC and ^1H NMR (>95% yield, maleate/fumarate = 13.8).

Catalytic Cyclopropanation of Styrene. A 167 μL portion of ethyl diazoacetate (1.607 mmol) was slowly added (ca. 1 h) via syringe to a well-stirred solution of 10 mg (10.7 μmol) of **1** and 828 μL (7.232 mmol) of styrene in dichloromethane. After it was stirred at room temperature for 15 min, the reaction mixture was analyzed by GC and ^1H NMR (85%; trans/cis 14/1). *anti*-ethyl 2-phenylcyclopropane-1-carboxylate: ^1H NMR ($CDCl_3$) δ 7.33−7.08 (m, 5H), 4.18 (q, 2H), 2.52 (m, 1H), 1.90 (m, 1H), 1.60 (m, 1H), 1.31 (m, 1H), 1.28 (t, 3H).

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Supporting Information Available: Tables of bond lengths, bond angles, general displacement parameter expressions, and positional parameters and figures showing the complete labeling of atoms (10 pages). Ordering information is given on any current masthead page.

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(29) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krûguer, C., Goddard, R., Eds.; Clarendon Press: Oxford, U.K., 1985.

(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

(31) ENRAF-Nonius Molecular Determination Package; Delft University, Delft, The Netherlands. Current version: 1990.