Cyclopropanation of Olefins with Diazoalkanes, Catalyzed by Co^{II}(porphyrin) Complexes − A Synthetic and Mechanistic Investigation and the Molecular Structure of Co^{III}(TPP)(CH_2CO_2Et) (TPP = Dianion of *meso*-Tetraphenylporphyrin)

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Dedicated to Prof. Mauro Graziani on the occasion of his 65th birthday

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Cobalt(II) porphyrin complexes catalyze reactions between ethyl diazoacetate (EDA) and styrenes to give the corresponding cyclopropanes with *trans* selectivity. The reactions of other diazoalkanes and other olefins have also been carried out, and the mechanism of the reaction has been investigated. Kinetic data and stoichiometric reactions support the formation of a diazoalkane cobalt-porphyrin complex that reacts with the olefins to generate the cyclopropane. Diethyl maleate and fumarate are not formed in the presence of an excess of olefin. On treatment of EDA with Co^{II}(TPP) (TPP = dianion of *meso*-tetraphenylporphyrin) in the absence of the olefin, an alkyl cobalt(III) complex Co^{III}(TPP)(CH_2CO_2Et) was isolated, and its structure has been solved by X-ray diffraction.

Introduction

A vast number of investigations into metal complex-catalyzed cyclopropanations of alkenes with diazo compounds have recently been reported.[1] A variety of transition metal compounds have been employed as catalysts for diazo decomposition, and the most efficient compounds have been found to be based on copper[2] and rhodium.[3]

In the last few years, transition metal-porphyrin complexes of iron,[4] rhodium,[5] osmium,[6] and ruthenium[7−9] have been extensively employed as catalysts in the cyclopropanation of olefins and, in the case of ruthenium, excellent enantioselectivity was obtained in this reaction.

The mechanism of the metal−porphyrin-catalyzed reactions has also been investigated. Carbene complexes have always been implicated, and the molecular structures of these carbene complexes have in several cases been determined by X-ray diffraction. Carbene complexes of ruthenium-,[7,9b,10] iron-,[4a,11] and osmium-porphyrins[10b,12] are known. In the case of rhodium, while no stable carbene complex has been isolated from reactions involving diazo compounds, one has been spectroscopically characterized and its reactivity investigated.[13] A stable rhodium-porphyrin carbene complex has been obtained by a different route and crystallographically characterized, but its reactivity with olefins was not investigated.[14]

Recently we have reported on the catalytic activity of cobalt(II) porphyrin complexes in the amination reactions of olefins[15] and benzylic C−H bonds,[16] with aromatic azides as aminating agents. Since diazo compounds are isoelectronic with aryl azides, we considered that cobalt(II) porphyrin complexes may also act as catalysts for the cyclopropanation reaction, and the results of our studies are reported here.

To the best of our knowledge, this is the first time that cobalt(II) porphyrin complexes have been used as catalysts for cyclopropanation reactions, though cobalt(II) Schiff bases[17,18] and dioximato complexes[19] are excellent catalysts for the cyclopropanation of olefins. Several reports concerning stoichiometric reactions between cobalt porphyrins and diazo compounds have been published.[20−22] Both cobalt(III) and cobalt(II) porphyrin complexes have been used as substrates, but in the latter case the reactions were always performed in $CHCl_3$ and in air, so chloride-containing cobalt(III) complexes were obtained as products in any case. The chloride anion clearly derives from a radical activation of the solvent, and in the only reaction employing

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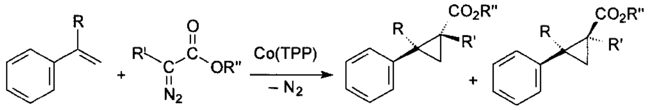
Co^{II}(OEP) and ethyl diazoacetate with exclusion of air, the same cobalt(III) chloride complex was obtained as in the presence of air, although after a longer time and in a lower yield.[20a] The identity of the major product depends on the amounts of the reagents and the identity of the diazo compound, but with ethyl diazoacetate the primary product from Co(OEP)[20a] or Co(TPP)[20b] was Co^{III}(porphyrin)(Cl)(CHCOOEt), with a carbene group bridging cobalt and one of the pyrrole nitrogen atoms. Relevantly to this work, all attempts to trap the carbene group by treatment with an olefin failed, indicating that the cobalt(III) carbene complex is not an active species in cyclopropanation reactions. No cyclopropanation activity has been reported even for the other complexes obtained under different experimental conditions or with other diazo compounds or porphyrins.

Results and Discussion

Catalytic Reactions

Ethyl diazoacetate reacts with an excess of olefin, in the presence of catalytic amounts of Co(porphyrin) complexes (1%), to give the corresponding cyclopropanes in good yields [Equation (1)]. The results are listed in Table 1. Fumaric and maleic acid esters were never detected in these reactions, consistently with literature data, which show that these by-products are not generally formed when catalytic systems based on cobalt complexes are employed.[17−19] It is also important to note that no polystyrene was formed either, as evidenced by the lack of any signal in the $-CH_2-$ region in the ^1H NMR spectra of reactions run in deuterated solvents (see also later).



(1)

The reaction between styrene (R = H) and EDA (R′ = H, R′′ = Et) in refluxing CH_2Cl_2, catalyzed by Co(TPP) (TPP = dianion of *meso*-tetraphenylporphyrin), gave a mixture of *trans*- and *cis*-cyclopropanes (**1**) in 85:15 ratio (Table 1, entry 1).

The most active catalyst for the synthesis of cyclopropanes, although slightly less diastereoselective as far as the *trans*/*cis* ratio is concerned, is Co(*p*-ClTPP) (*p*-ClTPP = dianion of *meso*-tetra-*p*-chlorophenylporphyrin) (entry 2). Co(*p*-OMeTPP) (*p*-OMeTPP = dianion of *meso*-tetra-*p*-methoxyphenylporphyrin) and Co(OEP) (OEP = dianion of *beta*-octaethylporphyrin) are also effective catalysts (entries 3 and 4).

With methyl phenyldiazoacetate (MPhDA, R′ = Ph, R′′ = CH_3) as the diazoalkane and again with styrene as the olefin and Co(*p*-ClTPP) as catalyst, a slower reaction was observed, as would be expected in view both of the greater stability of the starting diazo compound and of the steric hindrance of the derived carbene. The cyclopropane (**2**) was obtained in a 40% yield. Surprisingly, the most abundant cyclopropane isomer is the one with two phenyl groups in a *cis* arrangement (39:61 *trans*/*cis* ratio). The use of MPhDA will be investigated further, because many metal catalysts afford excellent *trans* selectivities,[2b,3,23] but only a few examples showing *cis* selectivity have been reported.[24]

With other diazoalkanes such as ethyl diazoacetacetate (EDAA, R′ = $COCH_3$, R′′ = Et) and with the diethyl ester of diazomalonic acid (EDM, R′ = COEt, R′′ = Et) we did not observe any reaction.

Other olefins were also tested. The reaction between 1,1-diphenylethylene (R = Ph) and EDA (R′ = H, R′′ = Et), catalyzed by Co(TPP), was fast and gave high yields of the cyclopropane (**3**, entry 5). With this olefin the most efficient catalyst appears to be Co(TPP), while Co(*p*-XTPP) (X = Cl, OMe) and Co(OEP) were less active and less selective. However the differences are not marked enough to allow any speculation about the electronic effects of the porphyrin ring. Again, with a hindered and more stable diazoalkane such as EDAA, a slower reaction was observed (**4**, 42% yield).

Table 1. Reactions of EDA with olefins catalyzed by Co^{II}(porphyrin)

Entry[a]	Substrate	Catalyst	t/h[b]	Cyclopropane yield%[c]	*trans*/*cis* ratio[d]
1	styrene	Co(TPP)	21	62 (**1**)	85:15
2	styrene	Co(*p*-ClTPP)	22	99 (**1**)	75:25
3	styrene	Co(*p*-OMeTPP)	22	80 (**1**)	76:24
4	styrene	Co(OEP)	24	71 (**1**)	83:17
5	1,1-diphenylethylene	Co(TPP)	7	99 (**3**)	−
6	1,1-diphenylethylene	Co(*p*-ClTPP)	10	88 (**3**)	−
7	1,1-diphenylethylene	Co(*p*-OMeTPP)	19	85 (**3**)	−
8	1,1-diphenylethylene	Co(OEP)	20	65 (**3**)	−
9	α-methylstyrene	Co(TPP)	19	95 (**5**)	70:30
10	α-methylstyrene	Co(*p*-ClTPP)	17	91 (**5**)	75:25
11	α-methylstyrene	Co(*p*-OMeTPP)	20	72 (**5**)	77:23
12	α-methylstyrene	Co(OEP)	21	65 (**5**)	85:15

[a] Reaction carried out in refluxing dichloromethane (10 mL), with $1.2 \cdot 10^{-3}$ mmol of catalyst and a catalyst/diazoalkane/styrene ratio of 1:100:500. [b] Time required to reach complete conversion of EDA. [c] Isolated yields, calculated with respect to the initial amount of the diazoalkane. [d] Determined by ^1H NMR spectroscopy.

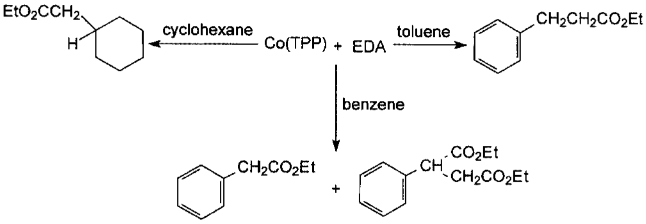
The reaction between α-methyl styrene (R = CH_3) and EDA, catalyzed by Co(TPP), gave good yields of the cyclopropanes (**5**, entry 9). The dominant isomer is the cyclopropane with the phenyl and the $-CO_2Et$ groups *trans* to each other. Small variations were observed on using the other porphyrin complexes as catalysts, while the use of the more hindered and stable EDAA gave slower reactions both when using Co(TPP) (**6**, 29% yield, 62:38 = *trans*/*cis* ratio) and when using Co(*p*-ClTPP) (**6**, 40% yield, 60:40 = *trans*/*cis* ratio).

The reactions between other olefins, such as norbornene and indene, and EDA with Co(*p*-ClTPP) as catalyst gave the corresponding cyclopropanes in low yields in mixtures with other compounds.

With 1-octene and cyclohexene, Co(*p*-ClTPP) as catalyst and EDA as the diazoalkane, we observed no derivatives originating from the attack of the carbene moiety on the alkene. On the other hand, we observed the products of coupling of two carbene units − that is, diethyl maleate and fumarate − for the first time. The formation of these coupling products when unreactive olefins are employed is in line with the results of the mechanistic study described below.

Preliminary studies were carried out with 2,3-dimethyl-1,3-butadiene as a representative diene. The efficiency of the catalytic system was checked under the same reaction conditions, and we observed the complete consumption of the EDA. Analysis of the ^1H NMR of the crude product verified the formation only of the monocyclopropanation derivative, and no coupling products were detected

Finally, when a 4:1 ratio between EDA and Co(TPP) was used, the products of the attack of the carbene on C−H bonds of the organic compounds used as solvent were observed in low amounts by GC-MS (Scheme 1).



Scheme 1

Intermolecular C−H activation by highly reactive metal carbenoid intermediates formed from diazo compounds has already been reported,[25] but alkylation of a C−H bond as stable as the one in benzene is rare.[26] These reactions will be investigated further.

Mechanistic Studies

The mechanism of the reaction between diazoalkanes and olefins with cobalt-porphyrins as catalysts was investigated by use of styrene as the olefin, EDA as the carbene precursor, and Co(TPP) as the catalyst. We first describe the experimental results and discuss them together in the end.

A series of kinetic measurements was performed; the reactions were followed by IR spectroscopy (disappearance of the absorptions of the diazo group at 2108 cm^{-1}), in benzene as solvent, at 50 °C. Some reactions showed an excellent first order dependence of the rate on the EDA concentration up to its complete consumption, but in several cases deviation from first order was observed after a variable time. We thus decided to calculate the kinetic constants for all reactions by the initial rates method (see also the Exp. Sect.). In all those cases in which first order behavior was observed throughout the reaction, good agreement was observed between the values obtained by the initial rates method and those obtained by fitting log[EDA] versus time for all the data points. The collected data show that the reaction rate is first order in EDA and in the catalyst (Figure 1 and Figure 2, see Exp. Sect.). In the latter case, the straight line in the plot of $k_{obsd.}$ versus the concentration of Co(TPP) showed an intercept on the axis of the concentration. The dependence of the reaction rate on the styrene concentration is more complex and has a bell shape, with styrene concentrations over 0.125 M inhibiting the reaction (Figure 3). Moreover, it has been observed that the diazoalkane is not completely consumed for concentrations of EDA higher than 0.05 mol/L.

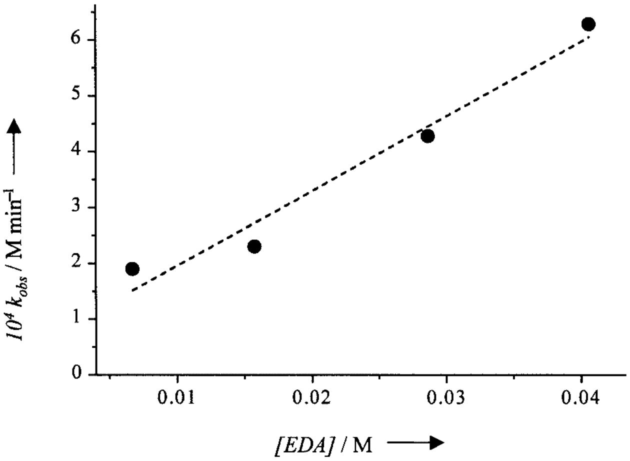


Figure 1. Dependence of the initial reaction rate on the initial EDA concentration; $k_{obsd.} = \{[EDA]_0 - [EDA]_t\}/t$, $R = 0.990$

One of the previously described experiments ($k_{obsd.}$ = 0.0149 min^{-1}) was repeated in the presence of several compounds capable of interfering with the formation of the cyclopropanes. In the presence of diethyl maleate ($k_{obsd.}$ = 0.0139 min^{-1}), diethyl fumarate ($k_{obsd.}$ = 0.0132 min^{-1}), and diethyl succinate ($k_{obsd.}$ = 0.0133 min^{-1}) the reaction rate is about 10% lower, but the reaction is still first order in EDA. This is probably due to the interaction of the metal center with the ester group of the added compound. In the absence of styrene, diethyl maleate reacts with EDA in the presence of Co(TPP) to give the corresponding cyclopropane in low yields. This last reaction is noteworthy, since it has never been reported with other catalytic systems based on metal-porphyrin complexes and it is usually performed with cobalt(0) or nickel(0) complex as catalyst.[27] On the

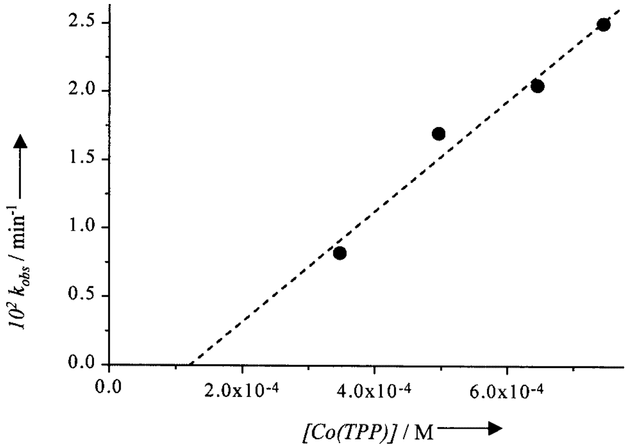


Figure 2. Dependence of the initial reaction rate on the initial Co(TPP) concentration; $k_{obsd.} = \{[EDA]_0 - [EDA]_t\}/[EDA]_0 \cdot t$, $R = 0.982$

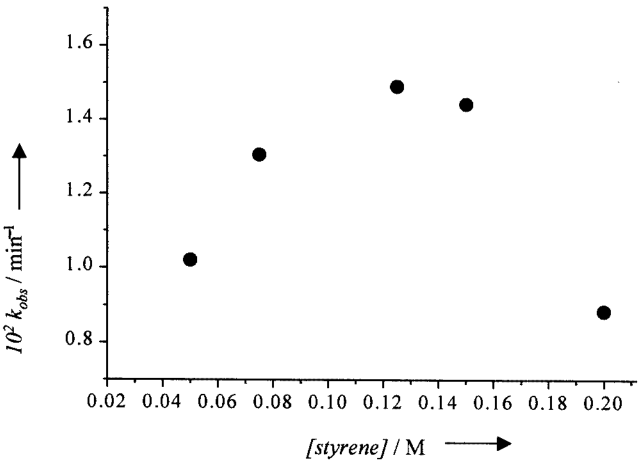


Figure 3. Dependence of the initial reaction rate on the initial styrene concentration; $k_{obsd.} = \{[EDA]_0 - [EDA]_t\}/[EDA]_0 \cdot t$

other hand, when dimethyl fumarate is used as substrate, only the cyclopropane derivative obtained from diethyl maleate (formed by carbene coupling from EDA) is obtained. This result emphasizes the importance of steric effects in this reaction. When we repeated the catalytic cyclopropanation reactions in the presence of the free radical trap TEMPO (2,2,6,6-tetramethylpyperidine-oxyl), we did not observe complete conversion of EDA, and a very slow reaction occurred. Since no irreversible reaction occurs between Co(TPP) and TEMPO alone,[16] this indicates that some intermediates in which unpaired spin density is present on the organic moiety must be formed during the reaction, although this should not be taken as an evidence of the formation of free organic radicals. An analogous outcome was observed for related amination reactions.[15,16]

Several reactions were performed in order to clarify the reaction mechanism. In the absence of the olefin and with use of a Co(TPP)/EDA ratio of 1:100, 35% of the EDA reacts to form diethyl maleate and a complex that has been identified as $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**). A different synthesis of this complex has previously been reported in the literature,[28] but the product was then only characterized spectroscopically. We have now unequivocally characterized complex **7** by X-ray crystallography, and its structure is described in the next section. It is important to note that **7** is inactive as a catalyst. It may be this species that explains why an intercept on the axis of the concentrations is observed on the plot of $k_{obsd.}$ versus the concentration of Co(TPP).

By carrying out the catalytic reaction in a ^1H NMR tube, with a Co(TPP)/EDA/styrene ratio of 1:10:50, we observed that if EDA is added first and then styrene, diethyl maleate is immediately formed, followed by the cyclopropane derivatives. On the other hand, if styrene is added first to the Co(TPP) solution and then EDA, only the cyclopropanes can be detected.

The stoichiometric reaction between Co(TPP) and EDA in the absence of styrene and at 50 °C in benzene was followed by IR spectroscopy, a spectrum being recorded every 10 minutes. It was possible to observe the steady disappearance of EDA ($\nu_{CO} = 1685\ cm^{-1}$) and, after 30 minutes, the formation of an absorption at 1722 cm^{-1}. This new signal is attributable to an unstable intermediate (**8**), since it gradually disappeared and at the end of the reaction only the absorptions due to diethyl maleate ($\nu_{CO} = 1730, 1750\ cm^{-1}$) and $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**) ($\nu_{CO} = 1710\ cm^{-1}$) were detected (Figure 4).

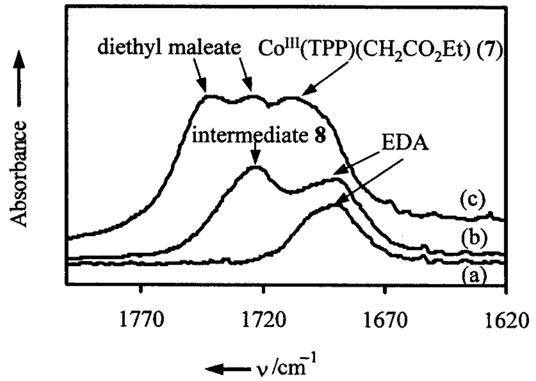


Figure 4. IR spectra of the reaction between Co(TPP) and EDA (stoichiometric ratio = 1:3); a) EDA; b) 30 min after the addition of Co(TPP); c) after 60 min (end of the reaction)

The absorption due to the diazo group at 2108 cm^{-1} gradually disappears, but no shift of this signal was detected. Even spectra subtraction techniques (Figure 5) failed to find any absorption attributable to a diazo group associated with the intermediate absorbing at 1722 cm^{-1}.

When the same reaction was run in C_6D_6 and followed by ^1H NMR spectroscopy, it was possible to observe the formation of a new paramagnetic species of cobalt(II) ($\delta = 22.2$ ppm) in the range from $\delta = 25$ to 10 ppm while the signals of Co(TPP) (13.2, 16.3 ppm) gradually disappeared (Figure 6).

As with the experiment followed by IR spectroscopy, only the signals of $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**) and diethyl maleate were observed at the end of the reaction. From these

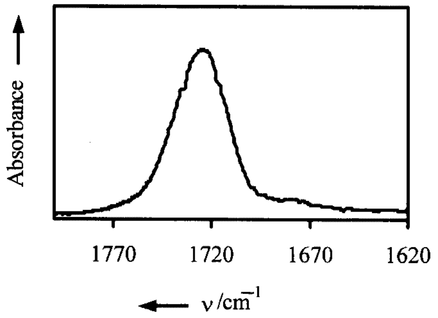


Figure 5. IR spectrum of the intermediate **8** obtained by subtracting spectrum (a) in Figure 4 from spectrum (b)

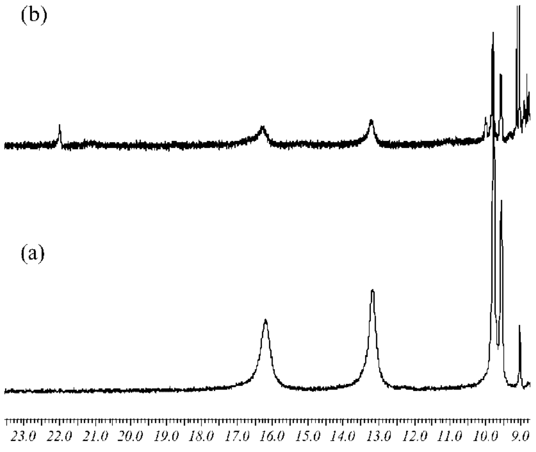
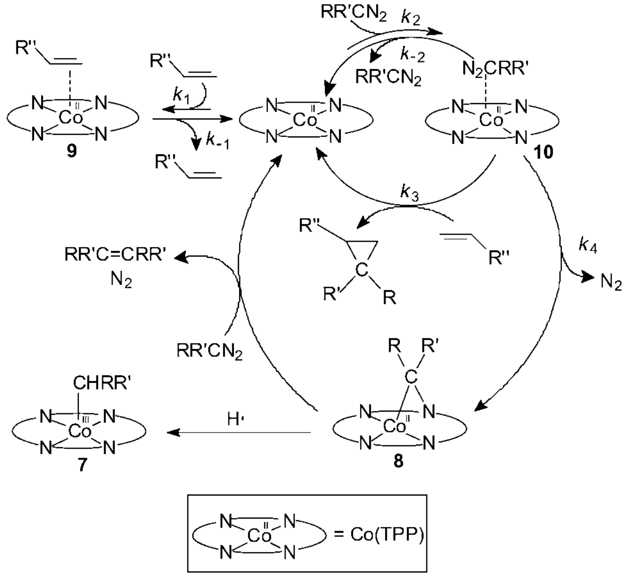


Figure 6. ^{1}H NMR spectrum of the reaction of Co(TPP) with EDA (stoichiometric ratio = 1:5). a) Co(TPP); b) 30 min after the addition of EDA

observations, we suggest that an intermediate carbene complex, $Co^{II}(TPP)(CHCO_2Et)$ (**8**), is formed. However, it was not possible to isolate it, since a fast reaction with EDA (to give diethyl maleate) occurs. We propose that the carbene group should be bridging between the cobalt and a pyrrole nitrogen atom, rather than being terminally bound only to cobalt, because related cobalt(III) complexes display this bonding mode,[20–22] and Tatsumi and Hoffmann's theoretical treatment of metalloporphyrin-carbene complexes[29] shows that an increase in the electron count on the metal stabilizes the bridging mode with respect to the terminal one. The bridging mode should thus be even more favorable for a cobalt(II) complex than for the cobalt(III) analogues. It should be noted that terminal cobalt(II) carbene complexes have been proposed as intermediates in cyclopropanation reactions catalyzed by cobalt Schiff base and dioximato ligands,[17–19] but these are different ligands and the formation of bridged complexes was apparently not taken into consideration.

The kinetic and reactivity data collected is not unequivocal in indicating the correct reaction mechanism. Given the observation of a transient carbene complex **8,** it is very tempting to point to this as the intermediate responsible for the production of both cyclopropane (by reaction with an olefin molecule) and diethyl maleate (by reaction with another EDA molecule). If this is the case, however, it is difficult to explain the bell-shaped dependence of the rate of cyclopropanation with the styrene concentration. The descending part of the curve may be due to competitive formation of a Co^{II}(TPP)(styrene) complex (**9**), inactive as catalyst, a mechanism for which there are precedents in related copper chemistry.[2a,30,31] In this case, however, explanation of the ascending part of the curve would require that the reaction between **8** and styrene proceed at a rate slower than, or at least comparable with, that of the formation of **8** itself. If this did not occur and the reaction between **8** and styrene were much faster than the formation of **8** from Co(TPP) and EDA, then the reaction rate should not depend on the styrene concentration and only the previously mentioned inhibiting effect should be observed. However, the assumption of a slow reaction between **8** and styrene contrasts with the failure to observe **8** in the presence of that olefin. We also tried to fit the kinetic data quantitatively to a model of this kind by a multivariate regression, but the results were inconsistent. In recent work in our laboratories[16] we have investigated the mechanism of the amination reaction of benzylic hydrocarbons by aryl azides. It turned out that the species responsible for the activation of the hydrocarbon is a reversibly formed complex in which the aryl azide is still coordinated as such, rather than a nitrene complex. By analogy, we can propose the mechanism shown in Scheme 2 for the cyclopropanation reaction.



Scheme 2

As shown in Scheme 2, the starting Co(TPP), which is in equilibrium with the catalytically inactive complex **9**, reacts with EDA to form the unstable intermediate **10**. This last complex can either react with the olefin to afford the cyclopropane derivative or lose dinitrogen to give the observed intermediate **8**. This is then responsible for the formation of diethyl maleate by reaction with an additional EDA molecule. The reaction with the olefin is much faster than the loss of dinitrogen, and the formation of the maleate is unobservable in the presence of an excess of olefin. Both of these reactions regenerate the active Co(TPP). Alternatively, complex **8** can be oxidized to the catalytically inactive Co^{III}(TPP)(CHRR′) (**7**). The source of the "hydrogen radical" necessary to transform **8** into **7** is uncertain, but it may be connected with a decomposition reaction of EDA. Indeed, **7** is formed more easily when a larger amount of EDA is present. We recall that incomplete consumption of the diazoacetate is observed at EDA concentrations higher than 0.05 M. This appears to be related to the formation of the catalytically inactive **7**. In this scenario styrene can either promote the reaction, by trapping the reversibly formed **10**, or inhibit it, by coordinating to Co(TPP) to form **9**. Formation of the cyclopropane even by reaction between the carbene complex **8** and styrene cannot be excluded, but it should not be the only route for its production.

To derive a kinetic equation for the process in Scheme 2 we can make the following assumptions:

a) The steady state approximation can be applied to intermediate **10**.

b) Coordination and de-coordination of the olefin are fast in comparison with the overall reaction. We call $K_{eq} = k_1/k_{-1}$.

c) The total concentration of cobalt at the beginning of the reaction (where data have been determined) is essentially the sum of the concentrations of Co(TPP) and **9**: $[Co]_{tot} = [Co(TPP)] + [\mathbf{9}]$.

d) The process associated with k_4 is slow with respect to that associated with k_3, in agreement with the selectivity data, and so can be neglected.

Under these assumptions the following kinetic equation is derived:

$$-d[EDA]/dt = k_2k_3[Co]_{tot}[EDA][styrene]/(k_{-2} + k_3[styrene])(K_{eq}[styrene] + 1)$$

which is in qualitative agreement with the observed trends, although the number of parameters and the limited number of data points available did not allow a more quantitative fitting.

Although Scheme 2 justifies all of the observed data, we must admit that a quite different mechanism is also consistent with the kinetic data. In this new scenario the intermediate reacting with ethyl diazoacetate would be Co(TPP)(styrene), presumably in equilibrium with both Co(TPP) and an inactive diolefin complex Co(TPP)$(styrene)_2$. A similar mechanism has been shown to operate in the case of a rhodium(III) porphyrin catalyst.[13c,13d] In the case of our system, we view the alternative mechanism as less likely, since no data, either collected by us or reported in the literature, supports the formation of a Co^{II}(porphyrin) complex with two olefins.

X-ray Structure of $Co^{III}(TPP)(CH_2CO_2Et)$ (7)

An ORTEP view of the $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**) molecule with the atom numbering used is shown in Figure 7. Selected interatomic distances and angles are reported in Table 2.

The complex consists of neutral molecules in which the trivalent cobalt atom is pentacoordinate through the four nitrogen atoms of the divalent TPP anion and one carbon atom of the $-CH_2CO_2Et$ moiety, and displays a distorted square-pyramidal coordination geometry. The four nitrogen atoms are coplanar within ± 0.08 Å, and the cobalt atom is displaced from this plane 0.108(1) Å towards the axial $-CH_2CO_2Et$ ligand. The average Co−N bond length is 1.957 Å, and is consistent with the range of nitrogen-cobalt bond lengths observed in five-coordinate organocobalt(III) com-

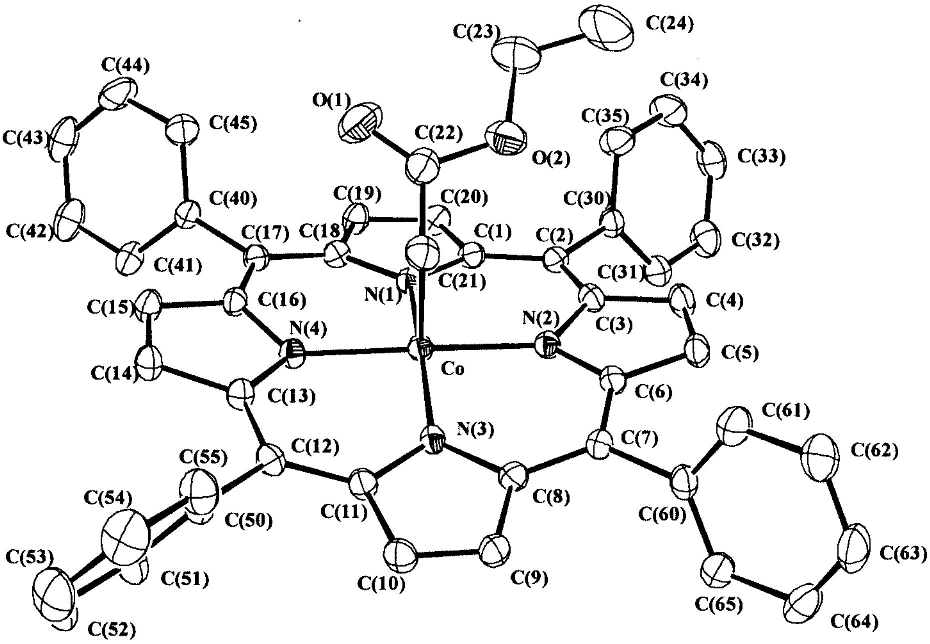


Figure 7. ORTEP drawing of the $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**) molecule; thermal ellipsoids are drawn at 30% probability

Table 2. Selected interatomic distances (Å) and angles (°) for $Co^{III}(TPP)(CH_2CO_2Et)$ (**7**)

Co−N(1)	1.962(2)	Co−N(2)	1.957(2)
Co−N(3)	1.952(2)	Co−N(4)	1.957(2)
Co−C(21)	2.013(3)	O(1)−C(22)	1.201(4)
O(2)−C(22)	1.364(4)	O(2)−C(23)	1.463(4)
N(1)−C(1)	1.389(3)	N(1)−C(18)	1.381(3)
N(2)−C(3)	1.386(3)	N(2)−C(6)	1.385(3)
N(3)−C(8)	1.389(3)	N(3)−C(11)	1.382(3)
N(4)−C(13)	1.383(3)	N(4)−C(16)	1.383(3)
C(1)−C(2)	1.373(4)	C(2)−C(3)	1.384(4)
C(6)−C(7)	1.382(4)	C(7)−C(8)	1.385(4)
C(11)−C(12)	1.383(4)	C(12)−C(13)	1.391(4)
C(16)−C(17)	1.378(4)	C(17)−C(18)	1.387(3)
C(21)−C(22)	1.438(5)	C(23)−C(24)	1.423(6)
N(1)−Co−N(2)	89.6(1)	N(1)−Co−N(3)	168.8(1)
N(1)−Co−N(4)	89.9(1)	N(1)−Co−C(21)	103.6(1)
N(2)−Co−N(3)	90.0(1)	N(2)−Co−N(4)	178.4(1)
N(2)−Co−C(21)	92.1(1)	N(3)−Co−N(4)	90.3(1)
N(3)−Co−C(21)	87.6(1)	N(4)−Co−C(21)	89.5(1)
C(22)−O(2)−C(23)	117.2(3)	Co−N(1)−C(1)	128.1(2)
Co−N(1)−C(18)	127.5(2)	C(1)−N(1)−C(18)	104.4(2)
Co−N(2)−C(3)	127.4(2)	Co−N(2)−C(6)	127.1(2)
C(3)−N(2)−C(6)	104.9(2)	Co−N(3)−C(8)	127.7(2)
Co−N(3)−C(11)	127.6(2)	C(8)−N(3)−C(11)	104.5(2)
Co−N(4)−C(13)	126.6(2)	Co−N(4)−C(16)	126.4(2)
C(13)−N(4)−C(16)	105.1(2)	N(1)−C(1)−C(2)	125.3(3)
N(1)−C(1)−C(20)	109.7(3)	C(2)−C(1)−C(20)	124.9(3)
C(1)−C(2)−C(3)	122.4(3)	C(1)−C(2)−C(30)	119.8(3)
C(3)−C(2)−C(30)	117.7(3)	N(2)−C(3)−C(2)	125.9(3)
N(2)−C(3)−C(4)	109.7(3)	C(2)−C(3)−C(4)	124.3(3)
N(2)−C(6)−C(5)	110.1(3)	N(2)−C(6)−C(7)	125.0(3)
C(5)−C(6)−C(7)	124.5(3)	C(6)−C(7)−C(8)	122.9(3)
C(6)−C(7)−C(60)	118.2(3)	C(8)−C(7)−C(60)	119.0(3)
N(3)−C(8)−C(7)	125.2(3)	N(3)−C(8)−C(9)	110.2(3)
C(7)−C(8)−C(9)	124.4(3)	N(3)−C(11)−C(10)	110.1(3)
N(3)−C(11)−C(12)	125.4(3)	C(10)−C(11)−C(12)	124.2(3)
C(11)−C(12)−C(13)	122.6(3)	C(11)−C(12)−C(50)	119.4(3)
C(13)−C(12)−C(50)	117.9(3)	N(4)−C(13)−C(12)	125.2(3)
N(4)−C(13)−C(14)	109.9(3)	C(12)−C(13)−C(14)	124.9(3)
N(4)−C(16)−C(15)	109.8(3)	N(4)−C(16)−C(17)	125.7(3)
C(15)−C(16)−C(17)	124.4(3)	C(16)−C(17)−C(18)	122.3(3)
C(16)−C(17)−C(40)	118.4(3)	C(18)−C(17)−C(40)	119.3(3)
N(1)−C(18)−C(17)	125.3(3)	N(1)−C(18)−C(19)	110.8(2)
C(17)−C(18)−C(19)	123.8(3)	Co−C(21)−C(22)	110.0(2)
O(1)−C(22)−O(2)	118.6(4)	O(1)−C(22)−C(21)	128.8(4)
O(2)−C(22)−C(21)	112.6(3)	O(2)−C(23)−C(24)	105.0(4)

plexes (1.948−1.969 Å).[32] The porphyrin core shows significant displacements of the atoms from the mean plane of the 24-atom core. The pattern of displacements conforms to an idealized D_{2d} symmetry with the pseudo-twofold axes passing through the methine carbon atoms C(2), C(12) or C(7), C(17) and the pseudo-dihedral mirror planes passing through N(1), Co, N(3) and N(2), Co, N(4).

The Co−C bond is 2.013(4) Å. Tetrahedral geometry is maintained at C(21) with a Co−C(21)−C(22) angle of 110.0(3)°; a significant distortion with respect to the ideal trigonal geometry is observed at C(22), the carbonyl carbon atom [C(21)−C(22)−O(2) 112.6(3)°, C(21)−C(22)−O(1) 128.8(4)°, O(1)−C(22)−O(2) 118.6(4)°], but the four-atom moiety is planar and the plane also includes atom C(23). The conformation of the $-CH_2CO_2Et$ axial appendage is such that the C(21)−C(22) bond almost projects onto the Co−N(1) bond. This orientation produces a C(21)−Co−N(1) angle [103.6(1)°] substantially larger than the other three C(21)-Co-N angles (see Table 2). A similar feature has also been observed in, for instance, (acetonyl)-Co(TPP).[33]

Experimental Section

General Procedures: Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere by use of standard Schlenk apparatus and magnetic stirring. Solvents were dried and distilled by standard procedures and stored under dinitrogen. TPP, *p*-ClTPP, *p*-MeOTPP[34] and their cobalt complexes[35] were synthesized by methods reported in the literature. All other starting materials, including Co(OEP), were commercial products and were used as received. Alkenes, EDA, EDAA, and EDM were purchased from Aldrich. MPhDA[36] was prepared as reported in the literature. Products **1**,[37] **2**,[38] **3**,[39] and **5**[40] have previously been reported in the literature and were characterized by comparison of their analytical data with those reported in the literature or obtained from independently synthesized samples. Gas chromatographic analyses were performed on a Dani 8610 capillary gas chromatograph equipped with a PS 255 column. Ri values (Ri = response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of the compounds of known concentrations. GC-MS analyses were performed on a Shimadzu GCMS-5000 instrument. NMR spectra were recorded on a Bruker AC 300 FT machine (300 MHz) at room temp. IR spectra were recorded on a Bio Rad FTS-7 FT-IR spectrophotometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Catalytic Reactions

The olefin (6.31 mmol) was added under an inert atmosphere to a solution of the diazo compound (1.26 mmol) and cobalt porphyrin catalyst ($1.26{\cdot}10^{-3}$ mmol) in CH_2Cl_2 (10.0 mL). The solution was heated at reflux with magnetic stirring. The reaction was run to complete consumption of the diazo compound (TLC analysis). The solvent was evaporated in vacuo and the products were purified by flash chromatography on silica gel. The determination of the molar ratio of the two diastereoisomers was carried out by ^{1}H NMR spectroscopy.

Compound 4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45−7.22 (m, 10 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 2.38 (s, 3 H), 2.21 (s, 1 H), 1.65 (s, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H)

Compound 6 *cis*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36−7.20 (m, 5 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 2.40 (s, 3 H), 2.25 (s, 1 H), 1.60 (s, 1 H), 1.27 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H)

Compound 6 *trans*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38−7.24 (m, 5 H), 4.02 (q, *J* = 7.2 Hz, 2 H), 2.37 (s, 3 H), 2.10 (s, 1 H), 1.81 (s, 1 H), 1.25 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H)

Kinetic Measurements

Co(TPP), styrene, and EDA were introduced in that order, under N_2, into a Schlenk flask. The flask was capped with a rubber septum and immediately placed in an oil bath, preheated at 50 °C. The solution was stirred for one minute to dissolve all reagents and a 0.20 mL sample of the solution was withdrawn for IR analysis. The consumption of EDA was monitored by IR spectroscopy (ν_{N2} = 2108 cm^{-1}). The apparent kinetic constants were calculated by use of the initial rate method. The data for different initial EDA concentrations were fitted to the equation $[EDA]_0 - [EDA]_t = k_{obs} \cdot t$, where $[EDA]_0$ and $[EDA]_t$ are the initial molar concentration of EDA and the molar concentration of EDA at the time t. The data for the series at different Co(TPP) or different styrene concentrations were fitted to the equation: $([EDA]_0 - [EDA]_t)/[EDA]_0 = k_{obs} \cdot t$.

i) Determination of the Kinetic Order with Respect to EDA: Co(TPP) (10.0 mg, $1.49 \cdot 10^{-2}$ mmol) was dissolved in benzene (30.0 mL) together with EDA (21 μL, 0.20 mmol) and styrene (0.430 mL, 3.75 mmol). The resulting red solution was heated at 50 °C. The consumption of EDA was monitored by recording an IR spectrum every 10 min ($k_{obsd.} = 1.90 \cdot 10^{-4}$ M min^{-1}). The same reaction was repeated three more times with three different amounts of EDA [a) 50 μL, 0.48 mmol, $k_{obsd.} = 2.30 \cdot 10^{-4}$ M min^{-1}; b) 90 μL, 0.86 mmol, $k_{obsd.} = 4.28 \cdot 10^{-4}$ M min^{-1}; c) 128 μL, 1.22 mmol, $k_{obsd.} = 6.29 \cdot 10^{-4}$ M min^{-1}].

ii) Determination of the Kinetic Order with Respect to Co(TPP): Co(TPP) (15.0 mg, $2.23 \cdot 10^{-2}$ mmol) was dissolved in benzene (30.0 mL) together with EDA (157 μL, 1.49 mmol) and styrene (0.430 mL, 3.75 mmol). The resulting red solution was heated at 50 °C. The consumption of EDA was monitored by recording an IR spectrum every 10 min ($k_{obsd.} = 2.62 \cdot 10^{-2}$ min^{-1}). The same reaction was repeated three more times with three different amounts of Co(TPP) [a) 13.0 mg, $1.94 \cdot 10^{-2}$ mmol, $k_{obsd.} = 1.85 \cdot 10^{-2}$ min^{-1}; b) 10.0 mg, $1.49 \cdot 10^{-2}$ mmol, $k_{obsd.} = 1.49 \cdot 10^{-2}$ min^{-1}; c) 7.0 mg, $1.0 \cdot 10^{-2}$ mmol, $k_{obsd.} = 0.76 \cdot 10^{-2}$ min^{-1}].

iii) Determination of the Kinetic Order with Respect to Styrene: Co(TPP) (10.0 mg, $1.49 \cdot 10^{-2}$ mmol) was dissolved in benzene (30.0 mL) together with EDA (157 μL, 1.49 mmol) and styrene (0.172 mL, 1.50 mmol). The resulting red solution was heated to 50 °C. The consumption of EDA was monitored by recording an IR spectrum every 10 min ($k_{obsd.} = 1.02 \cdot 10^{-2}$ min^{-1}). The same reaction was repeated four more times with four different amounts of styrene [a) 0.260 mL, 2.25 mmol, $k_{obsd.} = 1.31 \cdot 10^{-2}$ min^{-1}; b) 0.430 mL, 3.75 mmol, $k_{obsd.} = 1.49 \cdot 10^{-2}$ min^{-1}; c) 0.520 mL, 4.54 mmol, $k_{obsd.} = 1.44 \cdot 10^{-2}$ min^{-1}; d) 0.680 mL, 5.94 mmol, $k_{obsd.} = 0.88 \cdot 10^{-2}$ min^{-1}].

Typical Procedure for the ^{1}H NMR Analysis of the Reaction Progress: Co(TPP) (3.1 mg, $4.6 \cdot 10^{-3}$ mmol) was dissolved in C_6D_6 (0.75 mL) in an NMR tube. The substrates were added and the solution was then heated to 50 °C inside the probe. An NMR spectrum was recorded every five minutes.

i) EDA (4.7 μL, $4.5 \cdot 10^{-2}$ mmol) was added to a C_6D_6 solution of Co(TPP), and an NMR spectrum was immediately recorded, showing the presence of diethyl maleate (δ = 5.83 ppm, s 2 H, *-CH=CH-*). Styrene (26 μL, $2.3 \cdot 10^{-1}$ mmol) was then added to the mixture and the reaction was run to complete consumption of EDA. The progress of the reaction has already been described in the results and discussion section.

ii) Styrene (26 μL, $2.3 \cdot 10^{-1}$ mmol) was added to a C_6D_6 solution of Co(TPP), and an NMR spectrum was immediately recorded. No new peaks were detected, nor was any shift of those of Co(TPP) and styrene. EDA (4.70 μL, $4.47 \cdot 10^{-2}$ mmol) was then added to the mixture and the reaction was run to complete consumption of EDA. The progress of the reaction has already been described in the results and discussion section.

Stoichiometric Reaction between Co(TPP) and EDA

i) IR Analysis: Co(TPP) (10.0 mg, 1.49 10^{-2} mmol) and EDA (4.7 μL, 4.5 10^{-2} mmol) were dissolved in benzene (5 mL) at room temperature. The solution was heated at 50 °C and the consumption of EDA was monitored by recording an IR spectrum every 5 min. The progress of the reaction has already been described in the results and discussion section.

ii) ^{1}H NMR Analysis: Co(TPP) (3.2 mg, 4.8 10^{-3} mmol) was dissolved in C_6D_6 (0.75 mL) with CH_2Cl_2 (6.0 μL) as an internal standard. EDA (2.5 μL, 2.4 10^{-2} mmol) was then added to the mixture. The solution was heated at 50 °C and an NMR spectrum was recorded every 5 min. The progress of the reaction has already been described in the results and discussion section.

Preparation of $Co^{III}(TPP)(CH_2CO_2Et)$ (7): EDA (15.7 μL, $1.49 \cdot 10^{-1}$ mmol) was added under an inert atmosphere to a solution of Co(TPP) (100 mg, $1.49 \cdot 10^{-1}$ mmol) in CH_2Cl_2 (15.0 mL). The resulting red solution was stirred for 12 h at room temperature, by which time EDA had been completely consumed. The solution was evaporated to dryness under vacuum and the crude product was purified by chromatography on silica gel with CH_2Cl_2/*n*-hexane = 4:6 as eluent (68 mg, 60% yield). The analytical data (^{1}H NMR, IR, elemental analysis) are in agreement with the data reported in the literature.[22] Crystals suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2/*n*-hexane.

X-ray Structure Determination of $Co^{III}(TPP)(CH_2CO_2Et)$ (7): Crystal data: $C_{48}H_{35}CoN_4O_2$, f.w. 758.73, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.098(1)$, $b = 24.840(3)$, $c = 12.552(1)$ Å, $\beta = 116.11(1)$ °, $Z = 4$, $d_{calc} = 1.374$ Mg·m^{-3}, $\mu = 5.156$ cm^{-1}, $F(000)$ 1576. A crystal sample of dimensions 0.14 × 0.15 × 0.25 mm, obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution of the complex, was mounted on a glass fiber in air at room temperature on a Siemens SMART CCD area-detector diffractometer. Graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) was used, with the generator working at 50 *k*V and 35 mA. 31789 intensity data were measured in the full sphere (ω scan method) with sample-detector fixed at 5 cm, of which 6648 were independent; 2100 frames (20 s per frame, Δω = 0.3°) were collected and the first 100 frames were recollected for monitoring of crystal decay, which was not observed. An absorption correction was applied by use of the SADABS routine.[41] Transmission factors are in the 0.84−1.00 range. The structure was solved by direct methods (SIR, 97)[42] and refined with full-matrix, least- squares (SHELX93)[43] on the basis of 3113 independent reflections with $I > 2\sigma(I)$; $R = 0.036$, $R_{all} = 0.072$. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogens were riding on their carbon atoms. CCDC-190083 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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