Pergamon

Tetrahedron Letters 43 (2002) 3685–3687

TETRAHEDRON LETTERS

Cyclopropyl phosphonate ester synthesis catalyzed by ruthenium porphyrins: first characterization of a phosphonate carbene complex

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Accepted 27 March 2002

Abstract—Catalytic systems derived from Ru(CO)porphyrins are extremely efficient at converting styrene and diisopropyl diazomethyl phosphonate to cyclopropyl phosphonate esters in high yields and with high stereoselectivity; a monocarbene complex Ru(TPP)(CH{P(O)(O*i*Pr)$_2$}) has been isolated as a possible catalytically active species.

The metal-catalyzed cyclopropanation of olefins by diazo derivatives is frequently used in organic synthesis.[1] Most of these transformations involve metal–carbene species, but only in rare cases have these intermediates been spectroscopically detected.[2,3] Although diazoalkanes and diazoacetates are commonly used as reactive agents, very few reactions with diazomethylphosphonate have been previously reported with copper[4,5] or with rhodium complexes.[6] We previously reported the characterization and first X-ray structure of a porphyrin ruthenium carbene complex.[7] We now describe herein our results related to the reaction of diazomethylphosphonate with simple olefins catalyzed by ruthenium porphyrins and the characterization of the first porphyrin ruthenium complex with an axial phosphonate carbene ligand as a possible catalytically active species.

The complexes Ru(II)(por)(CO) (por = TPP, TMP, TPFPP)[8,9] in catalytic amounts, react with diisopropyldiazomethyl phosphonate (DAMP)[4] in the presence of an excess of styrene. The products are corresponding cyclopropyl phosphonate esters, obtained in very high yield (>90%) (Table 1) and with a very large excess of the *anti* isomer (Scheme 1). Catalytic cyclopropanations of alkenes were run in chloroform, at 40°C under an argon atmosphere, with a substrate:DAMP:catalyst ratio of 500:100:1. The diastereoselectivity (Table 1) is reminiscent of that observed with ruthenium catalysts[10] and ethyl diazoacetate (EDA), but differs from the *syn* selectivity observed with rhodium porphyrins.[11,12]

As shown in Table 1, the structure of the porphyrin is important since the use of the electrodeficient TPFPP instead of the unencumbered TPP core results in an increase from 12 to 104 of the *anti*:*syn* ratio of cyclopropyl-phosphonates. The *cis* and *trans* isomers of tetraisopropyl-ethene-1,2-diyl-bisphosphonate[13] are formed when the olefin does not react efficiently (Scheme 2). These coupling products are typically produced when the carbene transfer to the alkene is not observed. The *cis*/*trans* ratio for this dimer is 2.5/1 when Ru(TPP)(CO) is used as the catalyst. This is quite different from the large preference for diethyl maleate versus diethyl fumarate (15/1), which is observed for the dimerization of the carbene from EDA, using the same catalytic system.[14] The cyclopropane formation also exhibits a substrate shape preference, which may be useful for selective cyclopropanation of polyolefins.

Abbreviations: TPP = 5,10,15,20-tetraphenylporphyrin dianion; TMP = 5,10,15,20-tetramesitylphenylporphyrin dianion; TPFPP = 5,10,15,20-tetrapentafluorophenylporphyrin dianion; DAMP = diisopropyldiazomethyl phosphonate.

Keywords: catalysts; cyclopropanation; ruthenium complex.

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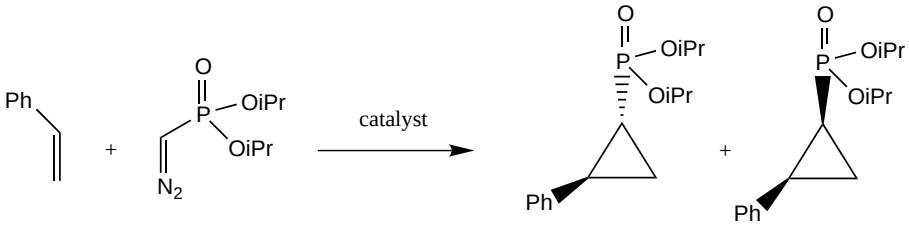
0040-4039/02/$ - see front matter
PII: S0040-4039(02)00612-3

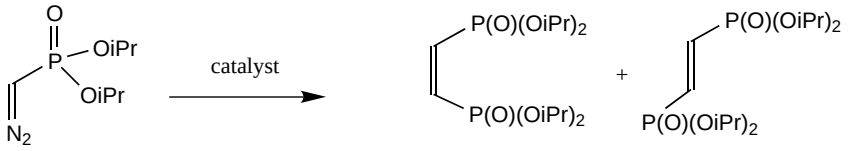
Table 1. Cyclopropanation of styrene derivatives by diisopropyl diazomethyl phosphonate using ruthenium porphyrin complexes as catalysts

Substrate	Catalyst	Ratio of *anti*:*syn* products[a]	Yield (%)[b]
Styrene	Ru(TPP)(CO)	12	90
–	Ru(TPFPP)(CO)	104	95
α-Methylstyrene	Ru(TPP)(CO)	17	80
–	Ru(TPFPP)(CO)	1	90
p-Methoxystyrene	Ru(TPP)(CO)	47	95
–	Ru(TPFPP)(CO)	316	95
p-Trifluoromethyl styrene	Ru(TPP)(CO)	4	93
–	Ru(TPFPP)(CO)	10	94

[a] Determined by GC–MS and ^{1}H NMR.
[b] Determined by GC–MS and ^{1}H NMR, based on diisopropyl diazomethyl phosphonate.



Scheme 1.



Scheme 2.

Thus, according to the amount of alkene formed in each reaction, styrene is cyclopropanated with high efficiencies, whereas α-methyl styrene is less reactive due to its encumbered double bound. Surprisingly, α-methyl styrene is cyclopropanated with a very low selectivity only when the electrodeficient TPFPP core is used.

The catalyst is also sensitive to the electronic nature of the olefin since aromatic alkenes are better substrates. For example, only traces of the cyclopropane products are detected when the reaction is carried out with cyclohexene. To obtain more information on the stereochemistry of the catalytical reaction a wide range of *para*-substituted styrene derivatives were tested; these results are reported in Table 1. As expected, electron-rich styrenes (4-methoxystyrene) are cyclopropanated more efficiently than styrene and alkenes bearing an electron-withdrawing group (4-trifluoromethylstyrene). As an example, a competition study of the cyclopropanation of 4-methoxystyrene and styrene gave a product ratio of 5 in favor of 4-methoxystyrene, when the catalyst is Ru(TPP)(CO) (Table 1). Thus, increasing the reactivity of the double bonds results in an enhancement of the *anti*/*syn* ratio. In contrast, it must be noted that we have recently shown that the diastereoselectivity of the cyclopropanation decreases with electron-rich styrenes using the catalytic system but using EDA[15] instead of DAMP.

Previous work demonstrated that ruthenium porphyrin carbenes obtained from diazoacetate are catalytically active.[10] We therefore presume that the active intermediate in the ruthenium porphyrin-catalyzed reactions is a ruthenium carbene species formed by reaction of ruthenium(II) with DAMP. Actually, when the reaction is monitored at room temperature, a Ru(II) carbene complex is detected by ^{1}H NMR when Ru(TPP)CO, Ru(TMP)(CO) or Ru(TPFPP)(CO) is used as the catalyst. For example, reaction of the carbonyl compound Ru(TPP)(CO) with a slight excess of DAMP in chloroform results in the displacement of the CO ligand and generation of the dark-brown carbene derivative Ru(TPP)(CHP(O)(O*i*Pr)$_2$) in 80% yield after 20 min at 40°C. The carbene derivative is stable in solution for at least 3 days under argon, and soluble in common polar organic solvents.

The new product has been characterized by conventional spectroscopic techniques. In particular, the ^{13}C NMR spectrum shows a typical low field signal for the carbene–carbon at 290 ppm, and ^{1}H NMR spectroscopy reveals a chemical shift for the α-carbon pro-

ton of the carbene fragment at 15 ppm† as a doublet due to phosphorus coupling ($J=49$ Hz). The two methyl groups of the bound ligand are diastereotopic and appear at 0.36 and −0.47 ppm as a doublet ($J=3.6$ Hz). These two resonances are shifted upfield relative to those of the free DAMP at 1.34 and 1.36 ppm, 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 6 nm blue shift. The new carbene complex obtained is also characterized by mass spectrometry (FAB).

In conclusion, this work which presents the first characterization of a phosphonate carbene complex also establishes the potential of such reagents (which are more easily handled than their air-sensitivity iron(II) porphyrin analogs) as efficient catalysts of cyclopropylphosphonate ester formation. Therefore, these compounds should also have potential application in organic synthesis.[16]

Acknowledgements

The authors are grateful to A. Bondon and S. Sinbandhit for their technical assistance and helpful discussions.

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† Based on diisopropyl diazomethyl phosphonate conversion. In a typical experiment, DAMP (0.25 mmol) is added to a vigorously stirred solution of the ruthenium catalyst (2.6 μmol) and alkene (1.25 mmol) at 40°C under an inert atmosphere. The reaction mixture is then stirred for 48 h and the cyclopropyl phosphonate ester formation is analyzed by GC-Mass.

Selected spectral data: **Ru(TPP)(CHP(O)(O*i*Pr)$_2$)**: ^{1}H NMR ($CDCl_3$): δ 15.2 (carbene C*H*, d $^2J_{PH}=49$ Hz, 1H), 8.6 (*Hβ pyrrole*, s, 8H), 8.2 (H_o, m, 8H), 7.8 ($H_{m,p}$, m, 12H), 2.2 ($(CH_3)_2CH$, m, 2H), 0.4 and −0.5 ($CH(CH_3)_2$, 2d $J=4$ Hz, 12H); ^{13}C NMR ($CDCl_3$): δ 290 ($J_{CP}=160$ Hz, carbene *C*); ^{31}P NMR ($CDCl_3$): δ 18.9 ($P(O)(OiPr)_2$); UV–vis: 406 nm (Soret); FAB: $m/z^+=893.2$. **Ru(TMP)(CHP(O)(O*i*Pr)$_2$)**: ^{1}H NMR ($CDCl_3$): δ 15.3 (carbene C*H*, d $^2J_{PH}=46$ Hz, 1H), 8.3 (*Hβ*, s, 8H), 7.2 ($H_{m,m'}$, 2s, 8H), 2.7 ($(CH_3)_2CH$, m, 2H), 2.7 ($CH_{3,p}$, s, 12H), 2.1 and 1.7 ($CH_{3,o,o'}$, 2s, 24H), 0.2 and −0.4 ($CH(CH_3)_2$, 2d $J=6$ Hz, 12H); ^{13}C NMR ($CDCl_3$): δ 285 ($J_{CP}=145$ Hz, carbene *C*); ^{31}P NMR ($CDCl_3$): δ 13.8 ($P(O)(OiPr)_2$); UV–vis: 405 nm (Soret); FAB: $m/z^+=1060.4$. **Ru(TPFPP)(CHP(O)(O*i*Pr)$_2$)**: ^{1}H NMR ($CDCl_3$): δ 15.8 (carbene C*H*, d $^2J_{PH}=37$ Hz, 1H), 8.4 (*Hβ*, s, 8H), 2.2 ($(CH_3)_2CH$, m, 2H), 0.3 and −0.6 ($CH(CH_3)_2$, 2d $J=6$ Hz, 12H); ^{31}P NMR ($CDCl_3$): δ 17.3 ($P(O)(OiPr)_2$); UV–vis: 400 nm (Soret). **Diisopropyl (2-(*E*)-(*p*MeO)phenyl) cyclopropyl phosphonate**: ^{1}H NMR ($CDCl_3$): δ aryl system: 7.1 (d, 2H) and 6.9 (d, 2H), 4.75 ($CH(CH_3)_2$, m, 2H), 3.8 (OCH_3, s, 3H), 1.4 ($(CH_3)_2CH$, m, 12H), AA′BM system: 2.5 (m, $^3J_{HH}=5.6$ Hz (2H *anti*), $^3J_{HH}=8.8$ Hz (1H *syn*), $^3J_{HP}=15.9$ Hz, 1H, $pCH_3OC_6H_4CH$); 1.5 (m, $^3J_{HH}=8.8$ Hz (1H *syn*) $^3J_{HP}=19$ Hz); 1.2 (m, $^3J_{HH}=5.6$ Hz (1H *anti*) $^3J_{HP}=12$ Hz); 1.1 (CHP(O), m $^3J_{HH}=5.6$ Hz (2H *anti*), 1H); GC–MS: $m/z^+=312$, 228, 212, 148, 43.