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Amide-Based Nonheme Cobalt(III) Olefin Epoxidation Catalyst: Partition of Multiple Active Oxidants $Co^V{=}O$, $Co^{IV}{=}O$, and $Co^{III}{-}OO(O)CR$

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Abstract: A mononuclear nonheme cobalt(III) complex of a tetradentate ligand containing two deprotonated amide moieties, $[Co(bpc)Cl_2][Et_4N]$ (**1**; H_2bpc = 4,5-dichloro-1,2-bis(2-pyridine-2-carboxamido)benzene), was prepared and then characterized by elemental analysis, IR, UV/Vis, and EPR spectroscopy, and X-ray crystallography. This nonheme Co^{III} complex catalyzes olefin epoxidation upon treatment with *meta*-chloroperbenzoic acid. It is proposed that complex **1** shows partitioning between the heterolytic and homolytic cleavage of an O−O bond to afford $Co^V{=}O$ (**3**) and $Co^{IV}{=}O$ (**4**) intermediates, proposed to be responsible for the stereospecific olefin epoxidation and radical-type oxidations, respectively. Moreover, under extreme conditions, in which the concentration of an active substrate is very high, the Co−OOC(O)R (**2**) species is a possible reactive species for epoxidation. Furthermore, partitioning between heterolysis and homolysis of the O−O bond of the intermediate **2** might be very sensitive to the nature of the solvent, and the O−O bond of the Co−OOC(O)R species might proceed predominantly by heterolytic cleavage, even in the presence of small amounts of protic solvent, to produce a discrete $Co^V{=}O$ intermediate as the dominant reactive species. Evidence for these multiple active oxidants was derived from product analysis, the use of peroxyphenylacetic acid as the peracid, and EPR measurements. The results suggest that a less accessible $Co^V{=}O$ moiety can form in a system in which the supporting chelate ligand comprises a mixture of neutral and anionic nitrogen donors.

Keywords: catalysts · cleavage reactions · cobalt · epoxidation · high-valent species

Introduction

Because metalloenzymes efficiently catalyze biologically important oxygenation reactions under mild conditions, several transition-metal-based catalysts have been designed and used to mimic the efficient enzymatic O−O bond-activation and subsequent oxygenations .[1] Iron and manganese porphyrins and related Schiff base complexes appear among the most successful oxidation catalysts for the oxidation of a wide range of organic substrates,[1,2] whereas cobalt complexes of other planar tetradentate ligands, such as amido ligands, have been much less explored.[3]

Considerable interest is currently being paid to the chemistry of nonheme high-valent metal-oxo species ($M^{IV}{=}O$ or $M^V{=}O$: M = Fe or Mn) as they have been identified and/or implicated in the catalytic cycles of a number of nonheme metal-containing enzymes that activate or evolve dioxygen.[1,2,4] Although their structures and reactivities have, to some extent, been well characterized and studied, the high-valent cobalt-oxo species ($Co^V{=}O$ and $Co^{IV}{=}O$) have been much less explored.[5,6] This is probably because, to the right of iron in the periodic table, the oxidation states with four or fewer d electrons are known to be less accessible and because the reactions of cobalt complexes with hydroperoxides often proceed through free-radical types of oxidation reaction. In the literature, some cobalt(IV)-oxo species[5] and only a few cobalt(V)-oxo species[6] have been proposed to be the active intermediates for oxygen transfer in reactions mediated by compounds of cobalt with oxidants such as peracids and PhIO, and much is not known about their oxidative reactivity.

During our research on modeling mononuclear nonheme metal-containing enzymes, we have studied the chemistry of nonheme metal (Fe and Mn) complexes of biscarboxamide donor ligands[7] because these types of ligands are highly desirable due to their simple and inexpensive preparation. In addition, the chemical reactivity of these systems can easily

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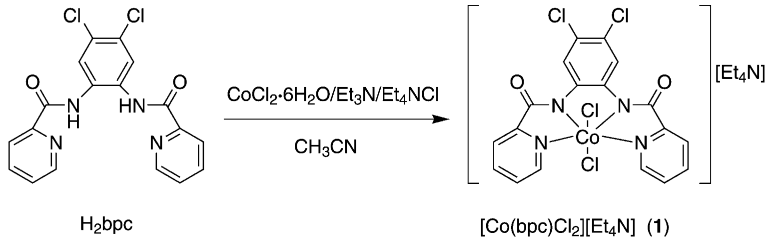
be tuned through modification of substituent groups at the pyridine ring or amide bridge. Moreover, as these ligands possess an overall dianionic charge (by deprotonation of the two amide moieties),[8] they might be expected to form high-oxidation-state metal complexes. Therefore, we recently reported on monomeric amide-based iron and manganese complexes that are capable of rapidly catalyzing the epoxidation of olefins by the use of *meta*-chloroperbenzoic acid (MCPBA), with high yields. Moreover, after using a mechanistic probe, the formation of the Fe^{V}-oxo, Mn^{V}-oxo, Mn^{III}-OO(O)CR, and Mn^{IV}-oxo moieties was proposed from the reactions of iron and manganese complexes with MCPBA as oxidant.[7] Accordingly, we expect that cobalt complexes with the same amide-based anionic chelating ligand could also produce the high-valent cobalt-oxo species.



Scheme 1. Synthesis of cobalt(III) complex **1**.

To extend the observations to nonheme cobalt complexes in an effort to develop efficient, selective, and readily available catalysts, to observe the less accessible high-valent cobalt-oxo species (Co^{V}=O or Co^{IV}=O), and to study the O–O bond cleavage mode of Co^{III}–OO(O)CR species and the catalytic reactivity, we synthesized and then characterized an amide-based nonheme Co complex and applied it to olefin oxidations with peracids as oxidants. We found that the Co complex catalyzed olefin epoxidation by MCPBA through multiple active oxidants.

Herein, we describe the synthesis and characterization of a new and easily accessible cobalt complex, and its reactivity toward oxidative functionalization of olefins by using MCPBA under mild conditions. It is important to note that mechanistic studies of the olefin epoxidation reactions promoted by this catalyst provide evidence that the cobalt complex shows partitioning between heterolytic and homolytic cleavage of the O–O bond to afford Co^{V}=O (**3**) and Co^{IV}=O (**4**) intermediates, proposed to be responsible for the stereospecific olefin epoxidation and radical-type oxidations, respectively. Moreover, under extreme conditions, in which the concentration of an active substrate is very high, the Co-OOC(O)R (**2**) species might be a possible reactive species for epoxidation. In protic solvents, the Co-OOC(O)R (**2**) species might undergo predominantly heterolytic cleavage to produce a Co^{V}=O species as the dominant epoxidizing intermediate.

Results and Discussion

The cobalt complex [Co(bpc)Cl_2][Et_4N] (**1**; H_2bpc = 4,5-dichloro-1,2-bis(2-pyridine-2-carboxamido)benzene) was synthesized by reacting equimolar amounts of $CoCl_2$·$6H_2O$ and the ligand H_2bpc in the presence of Et_3N/Et_4NCl in CH_3CN (Scheme 1; see the Experimental Section for details).[9] The absence of the $\tilde{\nu}$(N–H) stretching bands at approximately 3400–3150 cm^{-1} and the presence of the intense band at 1653 cm^{-1} in the IR absorption spectrum of the cobalt complex indicated that the coordinated amide ligand is deprotonated.[10] In the ^{1}H NMR spectrum, the appearance of proton peaks of the benzene and pyridyl rings at 7.90–9.76 ppm suggested that the complex **1** may have a low-spin Co^{III} oxidation state. Addition of diethyl ether to a reaction solution of **1** afforded dark brown crystals suitable for crystallographic analysis. The crystal structure of **1** revealed a coordination mode around the distorted octahedral metal center (Figure 1), similar to the structure of the bpb analogue.[9,11] The resultant cobalt complex is highly stable to air and moisture; it can be stored for several months in air without loss of catalytic activity.

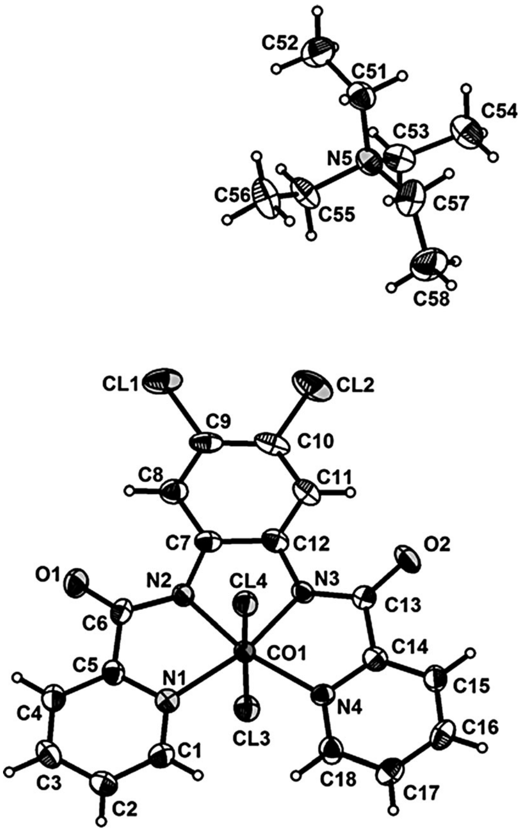


Figure 1. Crystal structure of complex **1**.

Catalytic epoxidation of various olefins by using MCPBA as a terminal oxidant with **1** as a catalyst was performed in a CH_2Cl_2/CH_3CN (1:1) solvent mixture at room temperature (see the Experimental Section for details).[12] We confirmed that direct substrate oxidation by MCPBA was negligible.[7,13] Addition of a further portion of MCPBA regenerated the catalytic cycle, with the same yield as the first cycle.

Cyclic olefins, such as cyclopentene, cycloheptene, and cyclooctene, were oxidized to the corresponding epoxides (48–64%; Table 1, entries 1–3), whereas the terminal olefin 1-octene was less efficiently oxidized to 1-octene oxide (Table 1, entry 4). Note that the reactions of cyclohexene afforded significant amounts of 2-cyclohexenone (7.3%) and 2-cyclohexene-1-ol (6.2%) as the allylic hydrogen abstraction products with cyclohexene oxide (43.6%) as a major product (Table 1, entry 5). This indicated that the radical-type oxidation reactions were, to a significant extent, involved in the olefin epoxidation reactions.[14] With cyclohexene under anaerobic conditions, almost identical yields of the products were obtained, thus indicating that oxygen molecules were not involved in the olefin epoxidation reactions. *cis*-2-Hexene and *cis*-2-octene were epoxidized to *cis*-2-hexene oxide (40.1%) and *cis*-2-octene oxide (46.3%) along with some amounts of *trans*-2-hexene oxide (11.1%) and *trans*-2-octene oxide (9.5%), which indicated moderate stereochemical retention (78 and 83%, respectively; Table 1, entries 6 and 8).[15] *trans*-2-Hexene and *trans*-2-octene were oxidized exclusively to *trans*-2-hexene oxide and *trans*-2-octene oxide in low yields (36.5 and 39.7%, respectively; Table 1, entries 7 and 9). In the competitive epoxidation of *cis*- and *trans*-2-octene, the ratio of *cis*- to *trans*-2-octene oxide was determined to be 1.3 (Table 1, entry 10). This value is similar to those observed with the MCPBA/$[(Fe(Me_2bpb)Cl_2]^-$ system ($k_{cis}/k_{trans} = 1.7$)[7a,9] and the MCPBA/$[(Mn(Me_2bpb)Cl(H_2O)]$ system ($k_{cis}/k_{trans} = 1.8$).[7c,9]

Table 1. Olefin epoxidations by MCPBA with cobalt catalyst **1** in CH_2Cl_2/CH_3CN (1:1) at room temperature.[a]

	Substrate	Product	**1**
1	cyclopentene	epoxide	48.4 ± 1.4
2	cycloheptene	epoxide	55.4 ± 1.2
3	cyclooctene	epoxide	63.9 ± 1.7
4	1-octene	epoxide	14.5 ± 0.2
5	cyclohexene	epoxide	43.6 ± 2.7
		2-cyclohexene-1-ol	6.2 ± 0.5
		2-cyclohexenone	7.3 ± 0.3
6	*cis*-2-hexene	*cis*-oxide	40.1 ± 4.5
		trans-oxide	11.1 ± 0.3
7	*trans*-2-hexene	*trans*-oxide	36.5 ± 1.2
8	*cis*-2-octene	*cis*-oxide	46.3 ± 9.6
		trans-oxide	9.5 ± 1.1
9	*trans*-2-octene	*trans*-oxide	39.7 ± 1.3
10	*cis*-/*trans*-2-octene	*cis*-/*trans*-oxide	1.3:1
11	styrene	epoxide	42.2 ± 1.4
		benzaldehyde	9.0 ± 0.1
		phenylacetaldehyde	8.3 ± 0.1
12	*cis*-stilbene	*cis*-oxide	21.1 ± 0.4
		trans-oxide	21.5 ± 0.5
		benzaldehyde	24.3 ± 0.0
13	*trans*-stilbene	*trans*-oxide	42.5 ± 1.4
		benzaldehyde	24.1 ± 0.5

[a] See the Experimental Section for details.

Aromatic olefins, such as styrene, *cis*-stilbene, and *trans*-stilbene, afforded significant amounts of aldehyde products: 17.3% (benzaldehyde and phenylacetaldehyde) for styrene, 24.3% for *cis*-stilbene, and 24.1% for *trans*-stilbene (Table 1, entries 11–13). This result suggests that significant amounts of cobalt(IV)–oxo species might be produced by the homolytic O–O bond cleavage of Co–OOC(O)R (**2**) species formed from the reaction of catalyst **1** and MCPBA.[5,16]

It has been proposed that some cobalt(IV)–oxo (**4**) species[5] and only a few cobalt(V)–oxo (**3**) species[6] are the active intermediates for oxygen transfer in reactions mediated by compounds of cobalt with oxidants such as MCPBA and PhIO,[5] whereas the reactions of cobalt complexes with hydroperoxides often proceed through free-radical types of oxidation reaction.[16] On the basis of the results presented herein and previously,[3,5,6,16] we propose that the cobalt complex promotes partitioning between heterolytic and homolytic cleavage of the O–O bond to afford $Co^V{=}O$ and $Co^{IV}{=}O$ intermediates, proposed to be responsible for the stereospecific olefin epoxidation and radical-type oxidations, respectively.[3,5,6]

To gain insight into the proposal that complex **1** promotes partitioning between the heterolytic and homolytic O–O bond cleavage of Co–OOC(O)R (**2**) species, we used peroxyphenylacetic acid (PPAA) as a mechanistic probe, because the cleavage mode could be easily determined by quantitative determination of the degradation products derived from PPAA.[7,17,18] Heterolytic cleavage of the O–O bond affords phenylacetic acid (PAA, **5**), and homolytic cleavage affords benzaldehyde (**6**), benzyl alcohol (**7**), and toluene (**8**) through the benzyl radical. Furthermore, the direct reaction of the acylperoxo intermediate and substrate affords PAA, and apparently affects the O–O bond cleavage mode. In the cyclohexene oxidation reaction catalyzed by **1** and PPAA, PAA was the dominant degradation product of PPAA (78.1% based on PPAA; Table 2, entry 1), with some amounts of benzaldehyde (11.3%) and benzyl alcohol (3.4%) generated from the homolytic O–O bond cleavage, thereby demonstrating that the Co–OOC(O)R species generated from the reaction of **1** and PPAA underwent partitioning of 84% heterolysis and 16% homolysis (Table 2, entry 1). To our knowledge, this is the first strong example of the formation of a $Co^V{=}O$ species that can be generated in nonheme cobalt complexes when using a peracid as the oxidant.[6,18]

On the other hand, as we and others have proposed, namely that the M–acylperoxo intermediate (M = Fe or Mn) might directly oxidize an olefin to an epoxide (when the substrate is active or the concentration of the substrate is high, the species M–OOC(O)R (**2′**) might be gradually involved in the epoxidation reaction),[7b,c,19] we examined the possibility of the direct olefin epoxidation by Co–OOR spe-

Table 2. Yield of products derived from PPAA mediated by cobalt catalyst **1** in the presence of various substrates.[a]

	Substrate	Heterolysis[b]	Homolysis[b]			Hetero/homo	Oxidation products[c]		
		5	**6**	**7**	**8**	[**5**/(**6**+**7**+**8**)]			
1	cyclohexene	78.1 ± 2.0	11.3 ± 0.4	3.4 ± 0.2	–	84:16	oxide (39.7 ± 1.7)	ol (8.6 ± 1.0)	one (7.3 ± 1.2)
2	*cis*-2-octene	75.3 ± 1.3	12.8 ± 0.3	3.0 ± 0.2	–	83:17	*cis*-oxide (34.5 ± 1.4)	*trans*-oxide (7.0 ± 0.2)	
3	1-octene	68.8 ± 3.1	14.7 ± 0.1	2.4 ± 0.1	–	80:20	oxide (12.3 ± 0.2)		

[a] Reaction conditions: substrate (0.5 mmol), catalyst (1.0×10^{-3} mmol), PPAA (0.02 mmol), solvent (1 mL, $CH_3CN/CH_2Cl_2 = 1{:}1$). [b] Based on PPAA; **5**–**8** indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [c] Based on PPAA; ol, one, and oxide indicate cyclohexenol, cyclohexenone, and the corresponding epoxide to each olefin, respectively.

Table 3. Yield of products derived from PPAA mediated by the catalyst **1** in the presence of 1-octene.[a]

	1-Octene [mM]	Heterolysis[b] **5**	Homolysis[b] **6**	**7**	**8**	Hetero/homo [**5**/(**6**+**7**+**8**)]	Oxidation products[c] 1-octene oxide
1	0	59.1 ± 4.2	12.1 ± 0.4	3.1 ± 0.8	–	80:20 (3.89)	0
2	50	58.9 ± 7.8	15.4 ± 0.2	2.7 ± 0.0	–	76:24 (3.22)	8.6 ± 0.2
3	100	71.6 ± 5.1	16.7 ± 0.3	2.7 ± 0.1	–	79:21 (3.69)	9.6 ± 0.2
4	200	71.7 ± 11.6	15.6 ± 1.1	2.6 ± 0.2	–	80:20 (3.94)	10.3 ± 0.4
5	500	68.8 ± 11.3	14.7 ± 0.4	2.4 ± 0.1	–	80:20 (4.02)	12.3 ± 0.2

[a] Reaction conditions: substrate (0–0.5 mmol), catalyst (1.0×10^{-3} mmol), PPAA (0.02 mmol), solvent (1 mL, $CH_3CN/CH_2Cl_2 = 1{:}1$). [b] Based on PPAA; **5**–**8** indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [c] Based on PPAA.

Table 4. Yield of products derived from PPAA mediated by the catalyst **1** in the presence of cyclohexene.[a]

	Cyclohexene [mM]	Heterolysis[b] **5**	Homolysis[b] **6**	**7**	**8**	Hetero/homo [**5**/(**6**+**7**+**8**)]	Oxidation products[c] oxide	ol	one
1	0	59.1 ± 4.2	12.1 ± 0.4	3.1 ± 0.8	–	80:20 (3.89)	0	0	0
2	50	61.0 ± 8.2	18.1 ± 0.3	2.5 ± 0.3	–	75:25 (2.96)	13.1 ± 0.0	5.2 ± 0.5	2.5 ± 0.5
3	100	65.1 ± 5.6	16.3 ± 2.1	3.4 ± 0.6	–	77:23 (3.30)	17.6 ± 0.6	4.8 ± 1.7	2.9 ± 0.2
4	200	71.8 ± 5.4	14.8 ± 0.1	3.3 ± 0.3	–	80:20 (3.97)	25.1 ± 3.0	6.5 ± 0.5	2.4 ± 2.4
5	500	78.1 ± 5.0	11.3 ± 0.6	3.4 ± 0.2	–	84:16 (5.30)	39.7 ± 0.9	8.6 ± 0.5	7.3 ± 0.1

[a] Reaction conditions: substrate (0.5 mmol), catalyst (1.0×10^{-3} mmol), PPAA (0.02 mmol), solvent (1 mL, $CH_3CN/CH_2Cl_2 = 1{:}1$). [b] Based on PPAA; **5**–**8** indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [c] Based on PPAA; ol, one, and oxide indicate cyclohexenol, cyclohexenone, and the corresponding epoxide to each olefin, respectively.

cies. We used two further substrates (an "easy one", *cis*-2-octene, and a "difficult one", 1-octene), and cyclohexene, to investigate the cleavage mode of PPAA with catalyst **1**. If the Co–OOR species was involved in the epoxidation reaction, then the ratio of heterolysis to homolysis would vary according to the type of substrate employed.[17a] The percentage of heterolysis to homolysis with catalyst **1** varied little within possible experimental error—from 84:16 for cyclohexene to 83:17 for *cis*-2-octene to 80:20 for 1-octene—as shown in Table 2 (entries 1–3). This selectivity appeared to be nearly independent of the substrate employed. The fact that the ratio of heterolysis to homolysis varied little with the substrate implies that there might be almost no interaction between the O–O bond cleavage and substrate oxidation.

To further examine the interplay between the O–O bond cleavage and substrate oxidation, we investigated the concentration effect of substrate, as previously shown by us and other groups.[7,17a] If the Co–OOR species was involved in the epoxidation reaction, then the ratio of heterolysis to homolysis would vary according to the concentration of substrate employed.[17a] First of all, we used two substrates that are difficult to oxidize, 1-octene and *trans*-2-octene. We increased the concentration of substrate 1-octene from 0 to 500 mM in the presence of catalyst **1**. The ratio of heterolysis to homolysis varied little within possible experimental error—from 80:20 (3.89) for 0 mM to 76:24 (3.22) for 50 mM to 79:21 (3.69) for 100 mM to 80:20 (3.94) for 200 mM to 80:20 (4.02) for 500 mM, as shown in Table 3 (entries 1–5). Similar product ratios were also observed for *trans*-2-octene (Table S1 in the Supporting Information). Next, we changed the substrates to more easily oxidized ones (cyclohexene and *cis*-2-octene).[20] With cyclohexene, the ratios of heterolysis to homolysis also varied only a little except for at 500 mM and were, within experimental error, from 80:20 (3.89) for 0 mM to 75:25 (2.96) for 50 mM to 77:23 (3.30) for 100 mM to 80:20 (3.97) for 200 mM to 84:16 (5.30) for 500 mM, as shown in Table 4 (entries 1–5). Similar results were also observed for *cis*-2-octene (Table S2 in the Supporting Information). These results suggest that Co–OOC(O)R (**2**) might be a possible reactive species for epoxidation under extreme conditions, in which the concentration of an active substrate is very high.

Additionally, we studied the solvent effects because it has been demonstrated previously that protic solvents facilitate O–O bond heterolysis to produce metal(V)–oxo species.[21] With complex **1**, the reaction conditions with 0.050 mmol cyclohexene were chosen to examine the product distribution of the mechanistic probe PPAA. As shown in Table 5 (entries 1–6), when the amount of the protic solvent CH_3OH was gradually increased from 0 to 20 %, the heterolysis was dramatically increased from 58 to 95 % to produce a possible reactive $Co^V{=}O$ species. These results suggest that partitioning between the heterolytic and homolytic O–O bond cleavage of PPAA is very sensitive to the nature of the solvent, and that the cleavage of the O–O bond of PPAA proceeds predominantly by heterolytic cleavage, even in the presence

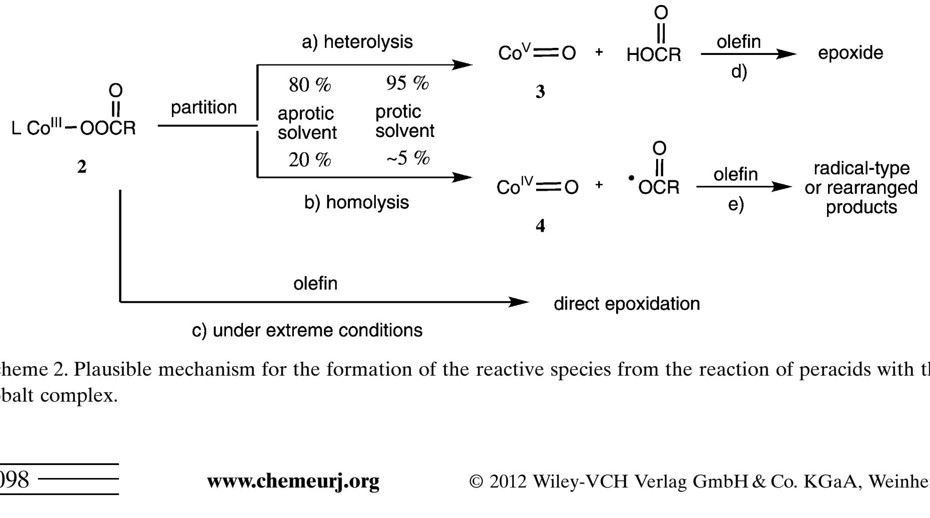
Table 5. Yield of products derived from PPAA mediated by the catalyst **1** in the presence of cyclohexene in protic solvent.[a]

	Solvent (MeCN/MeOH)	Heterolysis[b] **5**	Homolysis[b] **6**	**7**	**8**	Hetero/homo [**5**/(**6**+**7**+**8**)]	Oxidation products[b,c] oxide	ol	one
1	10.0:0	40.8 ± 2.6	26.0 ± 1.4	3.2 ± 0.2	–	58:42 (1.40)	8.8 ± 0.0	2.9 ± 0.1	2.3 ± 0.1
2	9.8:0.2	58.3 ± 2.6	16.9 ± 0.6	2.8 ± 0.1	–	75:25 (2.96)	7.3 ± 0.0	3.1 ± 0.5	2.3 ± 0.0
3	9.5:0.5	70.6 ± 2.1	6.0 ± 0.1	3.2 ± 1.0	–	88:12 (7.64)	5.1 ± 0.2	2.3 ± 0.0	1.9 ± 0.0
4	9.3:0.7	73.8 ± 4.0	3.8 ± 0.1	2.0 ± 0.1	–	93:7 (12.7)	6.8 ± 0.1	2.0 ± 0.0	1.5 ± 0.0
5	9.0:1.0	75.5 ± 2.2	2.8 ± 0.3	1.8 ± 0.1	–	94:6 (16.4)	8.2 ± 0.7	1.5 ± 0.0	1.2 ± 0.0
6	8.0:2.0	75.9 ± 0.5	2.7 ± 0.3	1.6 ± 0.0	–	95:5 (17.8)	7.5 ± 0.2	1.1 ± 0.1	1.1 ± 0.5

[a] Reaction conditions: cyclohexene (0.05 mmol), catalyst (1.0×10^{-3} mmol), PPAA (0.02 mmol), solvent (1 mL). [b] Based on PPAA. [c] Oxide, ol, and one indicate cyclohexene oxide, cyclohexenol, and cyclohexenone, respectively.

of small amounts of protic solvent, to produce a discrete $Co^{V}{=}O$ intermediate as the dominant reactive species.

Based on our results, the most plausible mechanism for the formation of the reactive species responsible for olefin epoxidation could be as shown in Scheme 2. Peracid reacts with a cobalt complex to form an initial cobalt–acylperoxo intermediate ($Co^{III}{-}OOC(O)R$ (**2**)), which then undergoes either a heterolytic (pathway a) or homolytic (pathway b) O−O bond cleavage to afford $Co^{V}{=}O$ (**3**) or $Co^{IV}{=}O$ (**4**) species in aprotic solvent ($CH_2Cl_2/CH_3CN = 1{:}1$). The resulting $Co^{V}{=}O$ intermediate formed from pathway a might be responsible for the olefin epoxidation that shows no formation of allylic oxidation products and a high stereochemical retention, whereas a $Co^{IV}{=}O$ complex generated with pathway b might be ascribed to a radical-type oxidation that shows the formation of allylic oxidation products and a loss of stereospecificity. In protic solvents, $Co^{III}{-}OOC(O)R$ (**2**) undergoes predominantly the heterolytic cleavage (pathway a) to produce a discrete $Co^{V}{=}O$ intermediate as the dominant reactive species. Additionally, under extreme conditions, in which the concentration of an active substrate is very high, **2** might be a possible reactive species for epoxidation (Scheme 2, pathway c). Therefore, under extreme conditions, even in our amide-based nonheme Co^{III}-catalyzed epoxidation reaction, the multiple oxidants $Co^{V}{=}O$, $Co^{IV}{=}O$, and $Co^{III}{-}OOC(O)R$ might act simultaneously as key active intermediates, as recently shown with the amide-based nonheme Mn^{III} complexes.[7b,c]



Scheme 2. Plausible mechanism for the formation of the reactive species from the reaction of peracids with the cobalt complex.

Next, we carried out a UV/Vis study at low temperature (−70 °C) to observe the proposed reactive intermediates: $Co^{III}{-}OOC(O)R$, $Co^{V}{=}O$, and $Co^{IV}{=}O$. As soon as 1.2 equivalents of MCPBA were added to a solution of **1** either in the absence of or in the presence of a substrate, cyclohexene, UV/Vis spectra were recorded within 3 s and then every 30 s over a period of 20 min (see Figure S1 in the Supporting Information). There was no spectral change at −70 °C, which suggests that the reactive intermediates might be spectroscopically not observable or present in concentrations too low to be detected.

In further efforts to detect the possible reactive species, we used the electron paramagnetic resonance (EPR) spectroscopy method at low temperature (−40 °C). As expected, the EPR spectrum of frozen solutions of complex **1** was silent. However, an intermediate state frozen as soon as complex **1** was mixed (for 5 s) with MCPBA at −40 °C in a mixture of MeCN and CH_2Cl_2 (1:1) showed clear EPR signals. There was a broad peak at a value of 5.28 g and a peak with eight lines at a value of 2.003 g (Figure 2), which might be because of the oxidation of a bpc ligand, $[Co^{III}(bpc^{ox})]^{2+}$ species. A similar spectrum was reported by Wieghardt et al.[11a,b,22] The spin state of the $[Co^{III}(bpc^{ox})]^{2+}$ species could be either a high-spin state ($S = {}^{3}\!/_{2}$) or a low-spin state ($S = {}^{1}\!/_{2}$) because cobalt(III) has a d^6 electronic configuration, but a g value of 5.28 clearly indicates that the spin state of this species should be a high-spin state. A possible explanation for these results is that $(bpc)Co^{IV}{=}O$ species generated from the homolysis of the $(bpc)Co{-}OOC(O)R$ intermediate might be in equilibrium with a $(bpc)Co^{III}$-coordinated ligand radical species, $[Co^{III}(bpc^{ox})]^{2+}$. Results obtained by using the mechanistic probe with PPAA, as described earlier, revealed that complex **1** showed partitioning between heterolysis (80 %) and homolysis (20 %) to afford EPR-silent $Co^{V}{=}O$ species and EPR-active $[Co^{III}(bpc^{ox})]^{2+}$ species, respectively. Therefore, we presume that the amounts of $[Co^{III}(bpc^{ox})]^{2+}$ species generated from the reaction of **1** and MCPBA might be much less than 20 %, although the exact amount of $[Co^{III}(bpc^{ox})]^{2+}$ species was not determined, because we did not observe any prominent UV/Vis change in the region 500–800 nm at −70 °C, which is the characteristic absorption region of the cation radical of the bpb ligand series.[11a,b,22]

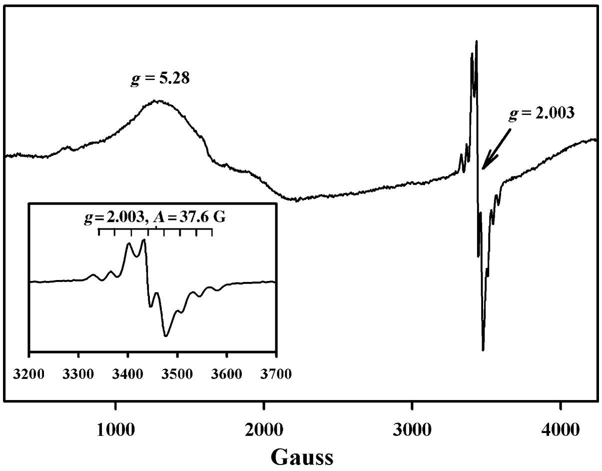


Figure 2. X-band EPR spectrum of $[Co^{III}(bpc^{ox})]^{2+}$ species generated in the reaction of $[Co^{III}(bpc)Cl_2]^-$ (**1**) with MCPBA in CH_3CN/CH_2Cl_2 (1:1) at −40 °C. Inset: EPR spectrum in the range of 3200–3700 G. The spectrum with eight lines in the inset clearly indicates the coupling of the bpc^{ox} radical species with the cobalt center ($I = 7/2$). Conditions: microwave frequency = 9.6465 GHz; microwave power = 1 mW; modulation frequency = 100 kHz; modulation amplitude = 10 G.

Conclusion

We have synthesized and characterized the mononuclear nonheme Co^{III} complex **1** supported by a chelate ligand having two deprotonated amide moieties. This complex catalyzes a wide range of olefin epoxidations by MCPBA, through multiple active oxidants $Co^{V}{=}O$, $Co^{IV}{=}O$, and Co^{III}–OOC(O)R.

It is proposed that **1** shows partitioning between heterolytic and homolytic cleavage of the O–O bond to afford both less accessible $Co^{V}{=}O$ and $Co^{IV}{=}O$ (or a Co^{III}-coordinated ligand radical) intermediates responsible for the stereospecific olefin epoxidation and radical-type oxidations, respectively. Moreover, under extreme conditions, in which the concentration of an active substrate is very high, the Co–OOC(O)R (**2**) is a possible reactive species for epoxidation. Furthermore, partitioning between the heterolytic and homolytic O–O bond cleavage of peracids is very sensitive to the polarity of the solvent, such that cleavage of the O–O bond of peracids proceeds predominantly by heterolytic cleavage in the presence of small amounts of protic solvent to produce a discrete $Co^{V}{=}O$ intermediate as the dominant reactive species. This proposal was explained after a reactivity study in which PPAA was used as a mechanistic probe.

These results and others recently reported by our group[7] reveal the important role that supporting chelate ligands having dianionic charge, through deprotonation of the two amide moieties, play in influencing the formation of high-valent metal–oxo species.

Experimental Section

General: Olefins, epoxides, cyclohexenol, cyclohexenone, methylene chloride, acetonitrile, diethyl ether, triethylamine, tetraethylammonium chloride hydrate, $CoCl_2{\cdot}6H_2O$, MCPBA (65 %), and $H_2{}^{18}O$ (95 % ^{18}O enrichment) were purchased from Aldrich Chemical Co. and were used without further purification. PPAA was synthesized according to the literature method.[7a] Product analyses for olefin epoxidation, partition reaction of PPAA, and ^{18}O incorporation reactions of cyclohexene oxide were performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with a Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a flame ionization detector and a 30 m capillary column (Hewlett–Packard, DB-5 or HP-FFAP). ^1H NMR spectra were recorded on a Bruker 250 instrument in $CDCl_3$ with TMS as the internal standard. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C instrument. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Low-temperature UV/Vis spectra were recorded on a Hewlett–Packard 8453 spectrophotometer equipped with an Optostat variable-temperature liquid-nitrogen cryostat (Oxford Instruments). EPR spectra were recorded on a Jeol JES-TE300 ESR spectrometer with 100 kHz field modulation.

Synthesis of cobalt complex (1): Ligand H_2bpc was synthesized as previously reported.[7a,23] $[Co(bpc)Cl_2][Et_4N]$ (**1**) was prepared by the reaction of $CoCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol) with H_2bpc (0.19 g, 0.5 mmol) in the presence of triethylamine (140 µL, 1 mmol) and tetraethylammonium chloride hydrate (0.17 g, 1 mmol) in MeCN (20 mL) at room temperature.[11c,d] For **1**, dark brown crystals suitable for X-ray analysis were obtained by layering diethyl ether on a solution of **1** in acetonitrile for 1 week at room temperature (yield: 0.21 g, 65.0 %); ^1H NMR ($[D_6]$DMSO, 400 MHz): $\delta = 9.76$ (d, 2H; pyridyl-H_6), 8.93 (s, 2H; benzyl-$H_{3,5}$), 8.24 (t, 2H; pyridyl-H_5), 8.03 (d, 2H; pyridyl-H_3), 7.90 ppm (t, 2H; pyridyl-H_4); IR (KBr): $\tilde{\nu} = 1653\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{26}H_{30}Cl_4CoN_5O_2$ $[Co(bpc)Cl_2][Et_4N]$ (**2**; 645.28): C 48.39, H 4.69, N 10.85; found: C 48.45, H 4.50, N 11.03.

X-ray analysis: The diffraction data for compound **1** were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled by using the Bruker–SAINT software package, and the structure was solved and refined with SHEXTL V6.12.[24] Hydrogen atoms were located in the calculated positions. The crystallographic data and selected bond lengths for compound **1** are listed in Tables S3 and S4 in the Supporting Information, respectively. CCDC-794826 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic olefin epoxidations by cobalt catalyst with MCPBA: MCPBA (0.02 mmol) was added to a mixture of substrate (0.5 mmol), cobalt catalyst (0.001 mmol), and solvent ($CH_3CN/CH_2Cl_2 = 1{:}1$, 1 mL). The mixture was stirred for 10 min at room temperature, even though the reaction was complete within a few seconds even at −40 °C. The reaction was monitored by GC/mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average product yields are presented. Product yields were based on MCPBA. In the competitive reactions of *cis*- and *trans*-2-hexene, and *cis*- and *trans*-2-octene, the concentration of the substrate was 0.25 mmol.

Analysis of the O–O bond cleavage products by cobalt catalyst with PPAA: PPAA (0.02 mmol) was added to a mixture of substrate (0–0.5 mmol), cobalt catalyst (0.001 mmol), and solvent ($CH_3CN/CH_2Cl_2 = 1{:}1$, 1 mL). The mixture was stirred for 10 min at room temperature. The reaction was monitored by GC/mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average product yields are presented. Product yields were based on PPAA. In a mixture of protic solvents (CH_3CN/CH_3OH), the same reactions were performed by gradually varying the amount of CH_3OH from 0 to 20 %.

UV/Vis spectroscopic studies: Solutions of **1** (0.03 mM) in CH_2Cl_2/CH_3CN (1:1, 3 mL) were first cooled to −70°C in a 1 cm UV cell. MCPBA (1.2 equiv, diluted in 30 μL CH_2Cl_2) was then injected into the UV cell in a single portion, whereupon the spectral changes were directly monitored within 3 s and at intervals of 30 s for 20 min by use of a UV/Vis spectrophotometer.

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[13] We confirmed that the direct epoxidation was negligible, because the oxygen transfer reaction catalyzed by **1** occurs in less than 5 s at room temperature and even at −40°C after peroxybenzoic acid ad-

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