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# Oxidative C–C Bond Cleavage of α-Keto Acids by Cobalt(II) Complexes of Nitrogen Donor Ligands

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Four cobalt(II) complexes,  $[(6Me_3TPA)Co^{II}(BF)](BPh_4)$  (1),  $[(TPA)Co^{II}(BF)](BPh_4)$  (2),  $[\{(6Me_3TPA)Co^{II}\}_2(PP)](BPh_4)_2$  (3), and  $[(TPA)Co^{II}(PPH)](BPh_4)$  (4) [where  $6Me_3TPA = tris(6-$ methyl-2-pyridylmethyl)amine, TPA = tris(2-pyridylmethyl)amine, BF = monoanionic benzoylformate, PP = dianionic phenylpyruvate, and PPH = monoanionic phenylpyruvate], of  $\alpha$ -keto acid derivatives have been isolated to show their versatile reactivity with dioxygen. The X-ray crystal structure of **2** suggests a five-coordinate cobalt(II) center coordinated by a monodentate benzoylformate and a tetradentate nitrogen-donor supporting ligand. Conversely, complex **3** is a dinuclear cobalt complex where two cobalt(II) centers are bridged by PP. While complex **1** is unreactive towards

## Introduction

a-Ketoglutarate-dependent dioxygenases constitute a large family of non-heme iron enzymes that catalyze the two-electron oxidation of organic substrates with concomitant decarboxylation of the  $\alpha$ -keto acid in the presence of dioxygen.<sup>[1-3]</sup> This class of enzymes is essential in many important biological functions such as DNA and RNA repair, biosynthesis of antibiotics, herbicide degradation, and oxygen sensing etc.<sup>[4-7]</sup> Despite their differences in biological function, this family of enzymes shares a common 2-His-1carboxylate facial triad motif at the active site.<sup>[8,9]</sup> It has now been established that an iron(II) center activates dioxygen to form an iron(IV)-oxo intermediate as the active oxidant to affect the substrate oxidation.<sup>[1,10-15]</sup> In biomimetic chemistry, several α-keto acid-iron(II) complexes of tetradentate ligands have been synthesized and characterized.<sup>[16-24]</sup> In most of the cases, benzoylformic acid or (phenyl)pyruvic acid have been used as model substrates that bind to the metal center with different binding motifs. These model complexes exhibit versatile reactivity towards

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Fax: +91-33-2473-2805 E-mail: ictkp@iacs.res.in dioxygen, **2** reacts slowly with oxygen to exhibit quantitative decarboxylation of coordinated benzoylformate to benzoate. An active cobalt-oxygen intermediate, intercepted by external substrates, is proposed to initiate the decarboxylation reaction. Complex **3** also reacts with dioxygen but to cleave the C2–C3 bond of PP with concomitant formation of benzaldehyde and an oxalate-bridged dicobalt(II) complex [ $\{(6Me_3TPA)Co^{II}\}_2(oxalate)](BPh_4)_2$  (5). The mononuclear PPH-cobalt(II) complex (4), unlike **2** and **3**, does not undergo oxidative decarboxylation or C–C bond cleavage of PPH. In the reaction with dioxygen, **4** is oxidized to a PP-cobalt(III) complex, [(TPA)Co<sup>III</sup>(PP)](BPh\_4) (**6**), as established from the X-ray single-crystal structure.

dioxygen and mimic the  $\alpha$ -ketoglutarate-dependent enzymes. Additionally,  $\alpha$ -keto acid substrate phenylpyruvic acid (PPH<sub>2</sub>) has relevance to a non-heme iron enzyme 4hydroxyphenylpyruvate dioxygenase (HPPD). HPPD catalyzes the conversion of 4-hydroxyphenylpyruvate to 2,5-dihydroxyphenyl acetate. Phenylpyruvate (PPH), unlike benzoylformate, tends to enolize depending upon the nature of the metal ion and on the supporting ligand. The enolization of PPH has been documented in iron(II) complexes of tetradentate nitrogen donor ligands. The iron(II)-phenylpyruvate complexes have been shown to undergo C-C bond cleavage of phenylpyruvate in the reaction with dioxygen.<sup>[24,25]</sup> Aliphatic C-C bond cleavage of substrates with enolate groups has been observed in β-diketone dioxygenase (Fe),<sup>[26-28]</sup> quercetin-2,3-dioxygenase (Cu)<sup>[29]</sup>, and acireductone dioxygenase (Ni).<sup>[30,31]</sup>

In some  $\alpha$ -ketoglutarate-dependent enzymes, it has been shown that the replacement of iron(II) by other divalent metal ions like Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, and Zn<sup>II</sup> leads to partial or complete loss of activity.<sup>[32]</sup> Recently, copper(I)–benzoylformate complexes have been shown to react with dioxygen to carry out oxidative decarboxylation of benzoylformate at low temperature in the presence of external substrates.<sup>[33]</sup> Compared to a large number of model  $\alpha$ -keto acid–iron(II) complexes presented in the literature,  $\alpha$ -keto acid complexes of other metal ions are rare. Studies on other metal complexes may provide additional information to understand the mechanism of dioxygen activation by model  $\alpha$ -keto acid

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complexes. With this objective we have investigated the reactivity of cobalt(II) complexes of  $\alpha$ -keto acid derivatives supported by tetradentate nitrogen donor ligands.

As a result of our investigation, we report herein the synthesis and characterization of four cobalt(II) complexes  $[(6Me_3TPA)Co^{II}(BF)](BPh_4)$  (1),  $[(TPA)Co^{II}(BF)](BPh_4)$  (2),  $[\{(6Me_3TPA)Co^{II}\}_2(PP)](BPh_4)_2$  (3), and  $[(TPA)Co^{II}-(PPH)](BPh_4)$  (4), where BF = benzoylformate anion, PP = dianionic phenylpyruvate enolate, and PPH = monoanionic phenylpyruvate (Scheme 1). The diverse reactivity of model complexes with dioxygen that lead to the oxidative C–C bond cleavage of  $\alpha$ -keto acids is discussed.



Scheme 1. Syntheses of cobalt(II) complexes.

### **Results and Discussion**

The cobalt(II) complexes were prepared by mixing the ligands with cobalt(II) salt and sodium salt of  $\alpha$ -keto acids. The complexes were isolated as tetraphenylborate or perchlorate salts (Scheme 1). All the complexes were characterized by several spectroscopic and analytical techniques including elemental analysis, FTIR, ESI-MS, and roomtemperature magnetic measurements. The IR spectrum of 1 exhibits  $v_{asym}(COO)$  and  $v_{sym}(COO)$  stretching frequencies at 1632 and 1450 cm<sup>-1</sup>, respectively, whereas those of **2** appear at 1634 and 1391 cm<sup>-1</sup>. Additionally, 1 and 2 show a carbonyl stretching (of the  $\alpha$ -keto group) frequency at 1672 and  $1688 \text{ cm}^{-1}$ , respectively. The spectroscopic data (see Supporting Information, Figure S1) suggest that the oxygen atom from the  $\alpha$ -keto group of benzoylformate remains noncoordinated in both the complexes. It appears from the carboxylate stretching frequencies that benzoylformate binds in monodentate fashion through one of the carboxylate oxygen atoms in 2 and in bidentate fashion via both the carboxylate oxygen atoms in 1.<sup>[34]</sup> IR spectrum of complex 4 exhibits carbonyl stretching frequency of phenylpyruvate at 1680 cm<sup>-1</sup>. The absence of this characteristic stretching vibration in complex 3 suggests a possible enolization of PPH (Scheme 1).

ESI-MS of mononuclear complexes 1, 2, and 4 (Figures S2 and S3) display molecular ion peaks at m/z = 540.36, 498.05, and 511.98 with isotopic distribution patterns calculated for  $[(6Me_3TPA)Co(BF)]^+$ ,  $[(TPA)Co(BF)]^+$ , and [(TPA)Co(PPH)]<sup>+</sup>, respectively. Dinuclear complex (3) exhibits an ion peak at m/z = 471.95 with an expected isotope distribution pattern for the complex cation [{(6Me<sub>3</sub>TPA)- $Co_{2}(PP)^{2+}$  (Figure S3). Ion peaks other than molecular ion peaks are observed in the mass spectra (Figures S2 and S3). Room-temperature magnetic moment values for the mononuclear complexes (1, 2, and 4) fall in the range 4.17– 4.94  $\mu_{\rm B}$ , indicative of the high-spin nature of the complexes. The magnetic moments are higher than those calculated for a spin-only high-spin d<sup>7</sup> ion, indicating a large orbital contribution to the magnetic moment. A lower value (6.35  $\mu_{\rm B}$ ) of magnetic moment than expected for two uncoupled cobalt(II) centers in 3 indicates that the cobalt(II) centers are exchange coupled. The complexes display d-d transitions in the visible region associated with the high-spin cobalt(II) complex (Figure S4). While the reported  $\alpha$ -keto acidiron(II) complexes of N<sub>4</sub> donor ligands exhibit iron(II)-toketo charge-transfer bands,<sup>[35]</sup> the cobalt(II) complexes (1, 2, and 4) do not display such charge-transfer bands. The optical spectroscopic data are consistent with the noncoordination of carbonyl oxygen from  $\alpha$ -keto acid in 1, 2, and 4. The optical spectra of cobalt(II)-benzoylformate complexes (1 and 2) differ in the position of d-d bands implying different ligand field strengths engendered by the supporting ligands. A higher intensity of the absorption bands in 2 is attributed to geometry less than octahedral symmetry (five-coordinate in 2 vs. six-coordinate in 1). An intense charge-transfer transition at around 330 nm is observed in the optical spectrum of 3 which may be assigned to cobalt(II)-PP interaction.

To investigate the compositions of cobalt(II)–benzoylformate complex **2** in solution, UV/Vis titration of [(TPA)- $Co^{II}(CH_3CN)$ ]<sup>2+[36]</sup> with sodium benzoylformate was carried out in acetonitrile at room temperature (Figure 1). It is very clear from the optical spectral changes during the titration that one equivalent of sodium benzoylformate is needed for maximum formation of **2**. No spectral change is observed upon further addition of benzoylformate. The



Figure 1. Optical spectral changes during the titration of [(TPA)- $Co^{II}(CH_3CN)$ ]<sup>2+</sup> in acetonitrile (c = 1 mM) with sodium benzoyl-formate.

absence of a metal-to-keto charge-transfer transition in the optical spectrum together with the analytical data support the binding of benzoylformate to the cobalt(II) center via a carboxylate oxygen atom in **2**.

To confirm the structures of mononuclear a-keto acidcobalt(II) complexes in solid state, efforts were made to grow the single crystals of 1, 2, and 4. Unfortunately, single crystals of 1 and 4 suitable for X-ray diffraction could not be isolated even after several attempts. However, from the analytical and spectroscopic data discussed above, and by analogy with a related cobalt(II)-salicylate complex<sup>[37]</sup> of the tetradentate 6Me<sub>3</sub>TPA ligand, a six-coordinate cobalt(II) complex with a bidentate binding motif of benzoylformate through both the carboxylate oxygen atoms may be proposed for 1. Conversely, single crystals of 2 were grown by vapor diffusion of diethyl ether into a solution of the complex in acetonitrile and tetrahydrofuran. The single crystal structure of 2 reveals a five-coordinate mononuclear complex cation where the metal ion is coordinated by four nitrogen donors from the ligand and one carboxylate oxygen (O1) of monoanionic benzoylformate (Figure 2).



Figure 2. ORTEP plot of the complex cation of 2 with 40% thermal ellipsoid parameters. The counterion and all H atoms are omitted for clarity.

The carbonyl oxygen O3 of benzoylformate is not coordinated to the metal center and supports the spectroscopic features in solution. Such a binding motif of benzoylformate has been observed in [(TPA)Fe<sup>II</sup>(BF)(MeOH)]<sup>+[16]</sup> and in  $[(Tp^{tBu,iPr})Fe^{II}(BF)]$   $[Tp^{tBu,iPr} = hydrotris(3-tert-butyl-5-tert-bu$ isopropyl-1-pyrazolyl)borate]<sup>[18]</sup> complexes. In 2, the amine nitrogen N3 of the ligand and the carboxylate oxygen O1 of benzovlformate occupy the axial positions with an N3-Co1-O1 angle of 170.95°(7), whereas three pyridine nitrogen atoms (N1, N2, and N4) of the ligand occupy the equatorial plane with N<sub>Py</sub>-Co-N<sub>Py</sub> angles ranging from 113.43°(7)–119.69°(7) (Table 1). A longer Co1····O2 distance of 3.263 Å clearly indicates the noncoordination of the carboxylate oxygen O2 with the metal center. This particular disposition of donor atoms constitutes a distorted trigonal bipyramidal coordination geometry ( $\tau = 0.85$ )<sup>[38]</sup> at the

cobalt(II) center. The bond parameters in **2** show resemblance to those reported in a five-coordinate cobalt(II) salicylate complex of the same ligand.<sup>[37]</sup>

Co(1)-O(1)	1.977(2)	Co(1)–N(1)	2.058(2)
Co(1) - N(2)	2.057(2)	Co(1) - N(3)	2.193(2)
Co(1)–N(4)	2.070(2)	C(19)–O(2)	1.222(3)
C(19)–O(1)	1.255(3)	C(20)–O(3)	1.207(3)
C(19)–C(20)	1.530(3)		
O(1)-Co(1)-N(1)	109.97(7)	O(1)-Co(1)-N(2)	93.75(7)
O(1)-Co(1)-N(3)	170.95(7)	O(1)-Co(1)-N(4)	102.02(7)
N(1)-Co(1)-N(2)	114.62(7)	N(1)-Co(1)-N(3)	78.08(7)
N(1)-Co(1)-N(4)	113.43(7)	N(2)-Co(1)-N(3)	78.80(7)
N(2)-Co(1)-N(4)	119.69(7)	N(3)-Co(1)-N(4)	77.68(7)

Conversely, the solid-state structure of 3 exhibits a dicobalt complex cation and tetraphenylborate counteranions. The dianionic phenylpyruvate (PP) forms a bridge between the two cobalt centers supported by the tetradentate ligand (Figure 3). In the asymmetric dimer, Co1 displays a six-coordinate distorted octahedral geometry with four nitrogen donors from the ligand and two oxygen donors (O1 and O2) from the dianionic phenylpyruvate. The other cobalt center Co2 has a five-coordinate distorted square-pyramidal ( $\tau = 0.47$ ) coordination geometry ligated by four nitrogen atoms of the ligand and the carboxylate oxygen O3. The complex cation is found to be isostructural with an iron(II) phenylpyruvate complex of the same ligand and all the bond lengths are close to the reported iron analogue.<sup>[24]</sup> The enolization of PPH upon coordination at the iron center is evident from the C44-O2 and C44-C45 distances of 1.318(3) and 1.360(3) Å, respectively (Table 2).



Figure 3. ORTEP plot of the cationic part of 3 with 40% ellipsoid probability. The tetraphenylborate counterion and all H atoms are omitted for clarity.

The reported cobalt(II) complexes of TPA, [(TPA)- $Co^{II}(CH_3CN)$ ](ClO<sub>4</sub>)<sub>2</sub>,<sup>[39]</sup> [(TPA)Co<sup>II</sup>(Cl)](ClO<sub>4</sub>), and [Co<sub>2</sub>(TPA)<sub>2</sub>( $\mu$ -tp)](ClO<sub>4</sub>)<sub>2</sub> (tp = dianionic terephthalate)<sup>[40]</sup> all exhibit five-coordinate distorted trigonal bipyramidal coordination geometry at the metal center. By analogy with

Table 2. Selected bond lengths [Å] and bond angles [°] for  $3 \cdot CH_2Cl_2$ .

Co(1)-O(1)	2.162(2)	Co(1)–O(2)	1.974(2)
Co(1)–N(1)	2.305(2)	Co(1) - N(2)	2.130(2)
Co(1)–N(3)	2.200(2)	Co(1)–N(4)	2.192 (2)
Co(2)–O(3)	1.978(2)	Co(2) - N(5)	2.161(2)
Co(2)–N(6)	2.135(2)	Co(2)–N(7)	2.161(2)
Co(2)–N(8)	2.076(2)	C(44) - O(2)	1.318(3)
C(44) - C(45)	1.360(3)	C(43) - O(3)	1.269(3)
C(43)–O(1)	1.258(3)	C(43) - C(44)	1.511(3)
O(2) - Co(1) - N(2)	168.61(7)	O(2) - Co(1) - O(1)	79.96(6)
N(2)–Co(1)–O(1)	88.66(6)	O(2)-Co(1)-N(4)	109.41(6)
N(2)-Co(1)-N(4)	81.75(7)	O(1)-Co(1)-N(4)	167.17(7)
O(2)-Co(1)-N(3)	102.80(7)	N(2)-Co(1)-N(3)	77.75(7)
O(1)-Co(1)-N(3)	91.17(6)	N(4)-Co(1)-N(3)	95.08(7)
O(2)-Co(1)-N(1)	102.64(7)	N(2)-Co(1)-N(1)	76.74(7)
O(1)-Co(1)-N(1)	90.41(7)	N(4)-Co(1)-N(1)	79.14(7)
N(3)-Co(1)-N(1)	154.40(7)	O(3)-Co(2)-N(8)	111.12(7)
O(3)–Co(2)–N(6)	165.29(7)	N(8)-Co(2)-N(6)	80.01(7)
O(3)–Co(2)–N(7)	92.78(7)	N(8)-Co(2)-N(7)	99.98(8)
N(6)-Co(2)-N(7)	75.37(8)	O(3)-Co(2)-N(5)	104.24(7)
N(8)-Co(2)-N(5)	109.82(8)	N(6)-Co(2)-N(5)	79.77(7)
N(7)-Co(2)-N(5)	136.82(8)		

the structure of **2** and of other cobalt(II) complexes of TPA, a five-coordinate PPH-cobalt(II) complex is expected for **4**. Moreover, the nature of the d-d band assigned for cobalt(II) and the stretching vibrations of the keto and carboxylate groups in the FTIR spectrum are comparable for both **2** and **4**. Furthermore, the cationic part of complex **4** (Figure 4) was optimized by DFT calculation which confirmed the five-coordinate geometry at the metal center. As in complex **2**, the metal ion is coordinated by four nitrogen donors of the tetradentate ligand and one of the carboxylate oxy-



Figure 4. DFT-optimized geometry of the cationic part of complex 4.

Table 3. Selected bond lengths [Å] and bond angles [°] of the DFT optimized geometry for complex 4.

Co-N(1)	2.0595	Co-N(2)	2.0488
Co-N(3)	2.2622	Co-N(4)	2.0789
Co-O(1)	2.0286	C(20)–O(3)	1.2290
C(20)–C(21)	1.5236	N(1)-Co-N(2)	109.466
N(1)-Co-N(3)	76.786	N(1)-Co-N(4)	108.783
N(2)-Co-N(4)	126.436	N(3)-Co-N(4)	77.759
O(1)-Co-N(1)	91.989	O(1)-Co-N(2)	107.082
O(1)–Co–N(3)	168.706	O(1)-Co-N(4)	107.569

gen atoms of the monoanionic phenylpyruvate. The C20–C21 distance of 1.524 Å and C20–O3 distance of 1.229 Å support the coordination of phenylpyruvate in the keto form. The bond parameters (Table 3) obtained from the optimized geometry are close to those of **2** and other reported five-coordinate cobalt(II) complexes.<sup>[37,39,40]</sup>

#### Reaction of Cobalt(II) Complexes with Oxygen

Unlike the iron(II)–benzoylformate complex of the tripodal 6Me<sub>3</sub>TPA ligand, the corresponding cobalt(II) complex **1** is unreactive towards dioxygen. Conversely, the five-coordinate cobalt(II)–benzoylformate complex **2** reacts with oxygen in acetonitrile slowly over a period of five days during which time the green solution turns orange. The final reaction solution exhibits an absorbance at 460 nm suggesting the formation of a low-spin cobalt(III) complex (Figure S5). Unfortunately, the final reaction solution exhibits a complicated <sup>1</sup>H NMR spectrum implying a mixture of species. However, ESI-MS of the reaction solution of **2** after two days displays an ion peak at m/z = 470.01 with the isotopic distribution pattern calculated for [(TPA)Co-(benzoate)]<sup>+</sup> which signify the oxidative decarboxylation of benzoylformate to benzoate during the reaction (Figure 5).



Figure 5. ESI-MS (positive ion mode in acetonitrile) of the solution after reaction of **2** with dioxygen. Inset: experimental and simulated isotope distribution patterns of the peak at m/z = 470.01.

To identify the organic products formed during the reaction with oxygen, acidic workup and subsequent <sup>1</sup>H NMR analysis of the oxygenated solution was carried out using the perchlorate salt of 2 (Figure 6). A quantitative conversion of benzoylformate to benzoate was observed after 5 d. Unfortunately, all attempts to isolate the oxidized complex from the reaction solution failed. It is important to mention here that no decarboxylation of benzoylformate was observed when a control experiment was carried out with a 1:1 mixture of cobalt(II) perchlorate and sodium benzoylformate under O2 in the absence of ligand. The benzoic acid formed in the reaction of 2 with  $O_2$  was esterified with  $\alpha$ -bromoacetophenone according to a reported procedure.<sup>[41]</sup> GC-MS of the ester derivative further confirms the formation of benzoic acid in the reaction of 2 with oxygen (Figure S6).



Figure 6. Formation of benzoic acid with time, monitored by <sup>1</sup>H NMR spectroscopy (500 MHz in CDCl<sub>3</sub> at 298 K), during the reaction of  $[(TPA)Co^{II}(BF)](ClO_4)$  (2·ClO<sub>4</sub>) with dioxygen. The peak marked as \* represents the resonance due to the *ortho* protons of the phenyl ring of benzoic acid and the # marked peak represents the residual solvent peak.

Conversely, the green solution of **3** in acetonitrile changes slowly under an oxygen atmosphere over a period of 7 h during which time the charge-transfer bands decay slowly (Figure 7). The decay of the charge-transfer band indicates the oxidative transformation of PP. This observation is in line with the PP-iron(II) complex of the same ligand. To understand the nature of PP cleavage products, the reaction solution after removal of metal ion was analyzed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR spectroscopic data confirms the formation of about 40% benzaldehyde.



Figure 7. Optical spectral changes during the reaction of 3 (0.1 mM) with dioxygen at room temperature. Inset: <sup>1</sup>H NMR spectrum of the reaction solution after removal of the metal ion.

ESI-MS of the final reaction solution exhibits a predominant peak at m/z = 435.15 with an isotope distribution pattern calculated for [{(6Me<sub>3</sub>TPA)Co<sup>II</sup>}<sub>2</sub>(oxalate)]<sup>2+</sup> (5) (Figure S7). ESI-MS and optical spectroscopic data suggest C–C bond cleavage of PP in the reaction with oxygen. The ESI-MS spectrum of the oxidized solution after reaction of **3** with <sup>18</sup>O<sub>2</sub> shows a predominant peak at m/z = 436.15along with a peak at 435.15 (Figure 8), indicating that one of the oxygen atoms of <sup>18</sup>O<sub>2</sub> is incorporated into oxalate. About 60% incorporation of <sup>18</sup>O into oxalate is calculated from the isotope distribution patterns of the peaks. The observed percentage of <sup>18</sup>O incorporation into oxalate may be attributed to the exchange of <sup>18</sup>O with residual water in the reaction medium.



Figure 8. ESI-MS (positive ion model in acetonitrile) of the solution after reaction of 3 with (A)  $^{16}O_2$ , (B)  $^{18}O_2$ .

To confirm the nature of the oxidized metal complex, Xray-quality single crystals of 5 were grown from a solvent mixture of dichloromethane and methanol. The solid-state structure of the dicationic complex (Figure 9) reveals a symmetrical oxalate-bridged dinuclear cobalt complex. The asymmetric unit contains only half of the overall dicationic unit. Two cobalt centers are symmetry related with an inversion point at the middle point of the oxalate C-C bond. Each of the cobalt is hexacoordinated by four nitrogen donors (N1-N4) of the ligand and two carboxylate oxygen atoms (O1 and O2) of the bridging oxalate ligand. The Co-N distances (Table 4) lie in the range 2.146(2)-2.225(2) Å whereas the Co1-O1 and Co1-O2 distances are 2.036(2) and 2.209(1) Å, respectively. The structure of the oxalatebridged dinuclear species bears resemblance to the reported iron(II) oxalate complex.<sup>[24]</sup>



Figure 9. ORTEP plot of the complex cation of **5** with 40% thermal ellipsoids. Hydrogen atoms and counterions have been removed for clarity.

The green solution of complex 4 in acetonitrile showing absorption bands at 304 nm and 322 nm slowly changes to an orange solution during the reaction with  $O_2$  for 3 h. ESI-MS (Figure 10, inset) of the orange solution displays a predominant molecular ion peak at m/z = 511.12 with an iso-

Table 4. Selected bond lengths [Å] and bond angles [°] for complex 5.

Co(1)-O(1)	2.036(2)	Co(1)–O(2)	2.209(2)
Co(1) - N(1)	2.175(2)	Co(1) - N(2)	2.146(2)
Co(1)–N(3)	2.225(2)	Co(1) - N(4)	2.203(2)
O(1)-Co(1)-N(2)	172.99(8)	O(1)-Co(1)-N(1)	104.79(8)
N(2)-Co(1)-N(1)	78.75(9)	O(1)-Co(1)-N(4)	97.44(7)
N(2)-Co(1)-N(4)	75.91(8)	N(1)-Co(1)-N(4)	98.96(7)
O(1)–Co(1)–O(2)	78.18(6)	N(2)-Co(1)-O(2)	98.39(8)
N(1)–Co(1)–O(2)	176.88(8)	N(4)-Co(1)-O(2)	81.47(7)
O(1)–Co(1)–N(3)	106.01(8)	N(2)-Co(1)-N(3)	79.08(8)
N(1)-Co(1)-N(3)	99.28(7)	N(4)-Co(1)-N(3)	145.33(9)
O(2)-Co(1)-N(3)	78.85(7)		

topic distribution pattern calculated for [(TPA)Co(PP)]<sup>+</sup> (Figure S7). The orange solution exhibits two strong absorptions at 322 nm and 335 nm (Figure 10).



Figure 10. Optical spectral changes of **4** (concentration: 0.5 mM) in the presence of molecular oxygen in acetonitrile at room temperature. Inset: ESI-MS of the oxidized solution of **4**.

Single crystals of the oxidized complex **6** were grown by vapor diffusion of diethyl ether into the reaction solution. The solid-state structure of the cationic complex (Figure 11) shows a mononuclear hexa-coordinate distorted octahedral cobalt complex ligated by four nitrogen donors (N1–N4) of the ligand and two oxygen atoms (O1 and O2) of the dianionic phenylpyruvate (PP). The amine nitrogen N2 and oxy-



Figure 11. ORTEP plot of the cationic part of complex 6 with 40% thermal ellipsoids. Hydrogen atoms and counterions have been removed for clarity.

gen donor O2 from phenylpyruvate occupy the axial positions with an N2–Co1–O2 angle of  $179.10(7)^{\circ}$ .

The enolization of coordinated PPH, upon oxidation of **4** with oxygen, is evident from the bond parameters. A shorter Co1–O2 bond with a length of 1.866(2) Å along with the double bond character of C20–C21 [length 1.344(3) Å] (Table 5) confirm the enolate character of the phenylpyruvate moiety coordinated to the cobalt center. The metal–nitrogen distances are in good agreement with low-spin cobalt(III) complexes.<sup>[37]</sup>

Table 5. Selected bond lengths [Å] and bond angles [°] for complex  $6^{\circ}2CH_3CN$ .

Co(1)-O(1)	1.880(2)	Co(1)–O(2)	1.866(2)
Co(1)–N(1)	1.921(2)	Co(1) - N(2)	1.944(2)
Co(1)–N(3)	1.917(2)	Co(1)–N(4)	1.921(2)
O(2)–C(20)	1.340(2)	C(20)–C(21)	1.344(3)
C(19)–O(1)	1.312(3)	C(19)–O(3)	1.223(3)
O(2)-Co(1)-O(1)	87.46(6)	O(2)-Co(1)-N(3)	94.60(7)
O(1)-Co(1)-N(3)	90.46(7)	O(2)-Co(1)-N(4)	93.98(7)
O(1)-Co(1)-N(4)	176.69(7)	N(3)-Co(1)-N(4)	92.39(7)
O(2)–Co(1)–N(1)	95.09(7)	O(1)-Co(1)-N(1)	89.21(7)
N(3)–Co(1)–N(1)	170.27(7)	N(4)-Co(1)-N(1)	87.70(7)
O(2)-Co(1)-N(2)	179.10(7)	O(1)-Co(1)-N(2)	91.68(7)
N(3)–Co(1)–N(2)	85.15(7)	N(4)-Co(1)-N(2)	86.89(7)
N(1)-Co(1)-N(2)	85.15(7)		

The two cobalt(II)–phenylpyruvate complexes react with dioxygen but afford different compounds (Scheme 2). While **3** undergoes oxidative C–C bond cleavage of PP, **4** is oxidized to form a PP-cobalt(III) complex upon loss of a  $C_{\beta}$ -H proton of PPH.

To investigate the mechanism of the reaction of cobalt(II) complexes with dioxygen, reactions were performed at low temperature. No intermediate species was observed in the optical spectrum at low temperature. The reaction of 2 with dioxygen was monitored by X-band EPR at 77 K using a superoxide trap DMPO.<sup>[42]</sup> Unfortunately, no EPR signal of the DMPO-superoxide spin adduct was observed. Therefore, interception studies were carried out with 2,4-ditert-butylphenol and 2,4,6-tri-tert-butylphenol to intercept oxygen-derived intermediate species involved in the reaction pathway (Scheme 3). The formation of cobalt(III) superoxide species in the reaction of cobalt(II) complexes with dioxygen is well established.<sup>[43]</sup> It is also known that the formation of biphenol from phenol takes place via H atom abstraction by a metal-superoxide intermediate followed by C–C coupling.<sup>[16,23,44–46]</sup> In the reaction of **2** with dioxygen, an almost stoichiometric amount of 4,4',6,6'-tetra-tert-butylbiphenol is formed as observed in the <sup>1</sup>H NMR spectrum of the organic product derived from 2,4-di-tert-butylphenol (see Exp. Section). An active oxygen species initiates the reaction via hydrogen atom abstraction to form an intermediate phenoxyl radical, which dimerizes immediately to form biphenol. Control experiments suggest that both the cobalt(II) complex and dioxygen are needed for the formation of biphenol from phenol.

The formation of 2,4,6-tri-*tert*-butylphenoxyl radical in a small amount as observed by X-band EPR spectroscopy during the reaction of **2** with 2,4,6-tri-*tert*-butylphenol and



Scheme 2. Reactivity of cobalt(II) phenylpyruvate complexes.



Scheme 3. Reaction of 2 with dioxygen in the presence of phenolic substrates.

subsequent decay of the radical species to 2,6-di-tert-butyl-1,4-benzoquinone further supports the involvement of an active cobalt-oxygen species (Figure S8).<sup>[47,48]</sup> Unlike in the case of 2, no evidence for the formation of 4,4',6,6'-tetratert-butylbiphenol or 2,6-di-tert-butyl-1,4-benzoquinone from the corresponding phenol was obtained in the reaction of other cobalt(II) complexes with dioxygen. Substrates like thioanisole, triphenylphosphane, and dimethyl sulfoxide have no effect on the oxidative decarboxylation of benzovlformate in 2, C–C bond cleavage of PP in 3, and β-hydrogen elimination from PPH in 4. Moreover, no oxo atom transfer occurs to these substrates with all the cobalt(II) complexes.

The bidentate binding of benzoylformate results in the formation of a coordinatively saturated cobalt(II) benzoylformate complex 1 which hampers the coordination of dioxygen and makes it unreactive. Conversely, in complex 2 oxygen can be activated at the vacant site to form a cobaltoxygen intermediate to initiate the oxidative decarboxylation of coordinated benzoylformate. The (6Me<sub>3</sub>TPA)Co<sup>II</sup> unit in **3** facilitates the enolization of PPH to coordinate as a dianionic ligand, whereas the  $(TPA)Co^{II}$  unit in 4 stabilizes the keto form of PPH. The C-C bond cleavage of PP in complex 3, upon reaction with dioxygen, proceeds via a dioxetane-type intermediate as proposed earlier for PP-iron(II) complexes of the 6Me<sub>3</sub>TPA ligand.<sup>[24]</sup> The reaction of complex 4 with dioxygen results in a cobalt(III) complex that spontaneously deprotonates the coordinated PPH to stabilize a PP-cobalt(III) complex, 6. The reaction of 2 and 3 with dioxygen is slower with respect to the corresponding iron analogues, however, the oxidative decarboxylation of benzoylformate is not inhibited by the TPA-cobalt(II) complex.

#### Conclusions

We have synthesized and characterized four cobalt(II) complexes using two different  $\alpha$ -keto acids. All the cobalt(II) complexes, except 1, react with molecular oxygen to exhibit a versatile reactivity pattern. The cobalt(II) benzovlformate complex 2 reacts with dioxygen to carry out oxidative decarboxylation of coordinated benzoylformate to benzoate. The dicobalt(II) complex 3 undergoes C-C bond cleavage of PP in the reaction with dioxygen to afford benzaldehyde and an oxalate-bridged dicobalt(II) complex 5. One of the oxygen atoms from molecular oxygen is incorporated into oxalate and the other oxygen possibly into benzaldehyde. The mononuclear PPH-cobalt(II) complex 4, in the reaction with dioxygen, forms a PP-cobalt(III) complex. Interception studies with external reagents suggest the involvement of an active cobalt-oxygen species in the decarboxylation of 2. The effect of supporting ligands together with the role of the metal ion in directing the reactivity of model cobalt(II) complexes have been demonstrated. The reactions described in this work have relevance in many C-C bond-cleaving dioxygenases.

### **Experimental Section**

Materials and Physical Measurements: Commercial-grade chemicals were used for synthetic purposes and solvents were distilled and dried before use. Although no problem was encountered during the synthesis of the complexes, perchlorate salts are potentially explosive and should be handled with care!<sup>[49]</sup> Air-sensitive complexes were prepared and stored in an inert atmosphere glove box. Ligands were synthesized according to the protocol reported in the literature.<sup>[50]</sup> Complex [(TPA)Co<sup>II</sup>(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> was synthesized following a reported procedure.<sup>[36]</sup>

Fourier transform infrared spectroscopy on KBr pellets was performed with a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed with a Perkin–Elmer 2400 series II CHN analyzer. Electro-spray ionization mass spectra were recorded with a Waters QTOF Micro YA263. <sup>1</sup>H NMR spectra were measured at room temperature with a Bruker DPX-500 spectrometer. Solution electronic spectra were measured with an Agilent 8453 diode array spectrophotometer. Room temperature magnetic data were collected on a Gouy balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contributions were estimated for each compound by using Pascal's constants. X-band EPR measurements were performed with a JEOL JES-FA 200 instrument.

**X-ray Crystallographic Data Collection and Refinement of the Structures:** Diffraction data for **2**, **3**·CH<sub>2</sub>Cl<sub>2</sub>, **5**, and **6**·2CH<sub>3</sub>CN were collected with a Bruker Smart APEX II (Mo- $K_a$  radiation,  $\lambda =$ 0.71073 Å). Details of the data collection and structure refinements are provided in Table 6. Cell refinement, indexing and scaling of the data set were carried out with the APEX2 v2.1-0 software.<sup>[51]</sup> The structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections.<sup>[52]</sup> In all the complexes the hydrogen atoms were fixed.

CCDC-865288 (for 2), -865289 (for 6·2CH<sub>3</sub>CN), -865290 (for 5), and -865291 (for 3·CH<sub>2</sub>Cl<sub>2</sub>) contain 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.

**DFT Calculations:** All calculations were performed with the Gaussian 03 program package.<sup>[53]</sup> The geometry of complex **4** was

optimized by spin unrestricted formalism using the BP86 functional.<sup>[54,55]</sup> Optimization was performed with all the coordinates using the 6-31G\* basis set for all the atoms except hydrogen, for which the  $6-21G^*$  basis set was used.<sup>[56]</sup>

**General Procedure for the Syntheses of BF-Cobalt(II) Complexes:** Cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) was added to a solution of the ligand (1 mmol) in methanol (5 mL). To the resulting solution sodium benzoylformate (0.17 g, 1 mmol) in methanol (2 mL) was added. The solution was then stirred at room temperature for 5 h. A solid compound was isolated from the reaction solution upon addition of 1 mmol sodium tetraphenylborate. The compound was then filtered, washed with methanol, and dried.

**[(6Me<sub>3</sub>TPA)Co<sup>II</sup>(BF)](BPh<sub>4</sub>) (1):** Yellow solid; yield 0.55 g (63%). **1**·H<sub>2</sub>O: C<sub>53</sub>H<sub>51</sub>BCoN<sub>4</sub>O<sub>4</sub> (877.74 g/mol): calcd. C 72.52, H 5.86, N 6.38; found C 72.61, H 5.68, N 6.22. IR (KBr):  $\tilde{v} = 3053$ , 3036, 2926 (m), 1672 (s), 1632 (s), 1607 (m), 1580 (m), 1450 (s), 1234 (m), 787 (m), 737 (s), 706 (s) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *mlz* (%) = 333.36 (30) [6Me<sub>3</sub>TPA + H]<sup>+</sup>, 540.36 (70) [(6Me<sub>3</sub>TPA)Co(BF)]<sup>+</sup>, 582.45 (100) [(6Me<sub>3</sub>TPA)Co(BF)(CH<sub>3</sub>-CN)]<sup>+</sup>. UV/Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  (ε, M<sup>-1</sup> cm<sup>-1</sup>) 390 (sh), 452 (sh), 568 (34) nm. Magnetic moment  $\mu_{eff}$  (298 K): 4.94 μ<sub>B</sub>.

**[(TPA)Co<sup>II</sup>(BF)](BPh<sub>4</sub>) (2):** Green solid. Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether into a tetrahydrofuran-acetonitrile solution of the complex; yield 0.65 g (79%). C<sub>50</sub>H<sub>43</sub>BCoN<sub>4</sub>O<sub>3</sub> (817.62 g/mol): calcd. C 73.45, H 5.30, N 6.85; found C 73.32, H 5.33, N 6.57. IR (KBr):  $\tilde{v} = 3051$  (m), 2986 (m), 1687 (m), 1633 (s), 1609 (s), 1576 (m), 1481 (s), 1431 (s), 1391 (s), 1230 (s), 766 (m), 733 (s), 706 (S) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): m/z (%) = 498.05 (100) [(TPA)-Co(BF)]<sup>+</sup>). UV/Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  (ε, m<sup>-1</sup>cm<sup>-1</sup>) 470 (220), 605 (160), 625 (sh) nm. Magnetic moment  $\mu_{eff}$  (298 K): 4.51 μ<sub>B</sub>.

[(TPA)Co<sup>II</sup>(BF)](ClO<sub>4</sub>) (2·ClO<sub>4</sub>): To a solution of cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) in acetonitrile (5 mL) was

Table 6. Crystallographic data for 2, 3·CH<sub>2</sub>Cl<sub>2</sub>, 5, and 6·2CH<sub>3</sub>CN.

	2	3·CH <sub>2</sub> Cl <sub>2</sub>	5	6·2CH <sub>3</sub> CN
Empirical formula	C <sub>50</sub> H <sub>43</sub> BCoN <sub>4</sub> O <sub>3</sub>	C <sub>100</sub> H <sub>96</sub> B <sub>2</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>8</sub> O <sub>3</sub>	C <sub>92</sub> H <sub>88</sub> B <sub>2</sub> Co <sub>2</sub> N <sub>8</sub> O <sub>4</sub>	C55H50BCoN6O3
Formula weight	817.62	1668.23	1509.18	912.75
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2(1)/c	ΡĪ	P2(1)/c	P2(1)/c
<i>a</i> [Å]	11.4009(8)	12.1803(7)	9.698(3)	16.3195(10)
<i>b</i> [Å]	9.0805(7)	16.2584(10)	17.644(5)	11.6310(7)
c [Å]	41.472(3)	21.9791(14)	24.316(6)	26.1992(13)
a [°]	90.00	89.732(2)	90.00	90.00
β[°]	103.840(2)	78.343(2)	112.469(9)	116.087(3)
γ [°]	90.00	88.092(2)	90.00	90.00
$V[Å^3]$	4168.8(5)	4260.4(4)	3844.9(19)	4466.3(4)
Z	4	2	2	4
$\rho_{\text{calcd.}}$ [Mg/m <sup>3</sup> ]	1.303	1.300	1.304	1.357
<i>T</i> [K]	298(2)	120(2)	150(2)	150(2)
$\mu$ Mo- $K_a$ [mm <sup>-1</sup> ]	0.460	0.509	0.491	0.438
F(000)	1708	1748	1584	1912
$\theta$ range [°]	1.01-26.01	4.20-29.86	1.47-21.47	1.39-27.92
Reflections collected	40580	68801	26168	48856
Reflections unique	8151	23574	4371	10511
<i>R</i> (int)	0.0487	0.0509	0.0489	0.0396
Data $[I > 2\sigma(I)]$	6228	16066	3509	8209
Parameters refined	532	1060	490	582
Goodness-of-fit on $F^2$	0.919	0.984	1.663	0.967
$R_1 [I > 2\sigma(I)]$	0.0403	0.0522	0.0343	0.0472
wR2	0.1183	0.1436	0.0498	0.1237
Residuals [eÅ <sup>-3</sup> ]	-0.404, 0.281	-1.488, 1.151	-0.218, 0.191	-0.857, 0.473

added a solution (5 mL) of the ligand (0.29 g, 1 mmol) in acetonitrile. To the resulting solution solid sodium benzoylformate (0.17 g, 1 mmol) was added and the resulting mixture was stirred for 5 h. The solution was concentrated to 1 mL and diethyl ether (10 mL) was added. The mixture was then stirred for 1 h to precipitate a green solid which was isolated by filtration, washed 2–3 times with diethyl ether, and dried; yield 0.45 g (76%). C<sub>26</sub>H<sub>23</sub>ClCoN<sub>4</sub>O<sub>7</sub> (597.87 g/mol): calcd. C 52.23, H 3.88, N 9.37; found C 52.54, H 3.79, N 9.57. IR (KBr):  $\tilde{v} = 3433$  (m), 2922–2853 (w), 1665 (m), 1609 (s), 1483 (m), 1441 (m), 1230 (s), 1144–1088 (vs), 771 (m), 631 (s) cm<sup>-1</sup>.

[{(6Me<sub>3</sub>TPA)Co<sup>II</sup>}<sub>2</sub>(PP)](BPh<sub>4</sub>)<sub>2</sub> (3): To a solution of the ligand (0.33 g, 1 mmol) in methanol (5 mL), cobalt (II) chloride hexahydrate (0.24 g, 1 mmol) in methanol (2 mL) was added. To the resulting solution was added solid sodium phenylpyruvate (NaPPH) (0.18 g, 1 mmol) and the solution was stirred for 5 h. Treatment of the solution with NaBPh<sub>4</sub> (0.34 g, 1 mmol) resulted in the isolation of a light green solid. Single crystals suitable for X-ray diffraction were grown from a solvent mixture of dichloromethane and methanol; yield 0.76 g (95%).  $3 \cdot CH_2Cl_2$ :  $C_{100}H_{96}B_2Cl_2Co_2N_8O_6$ (1668.23 g/mol): calcd. C 71.99, H 5.80, N 6.72; found C 71.82, H 5.83, N 6.79. IR (KBr):  $\tilde{v} = 3053$  (s), 2984 (m), 2920 (m), 1607 (s), 1576 (s), 1537 (s), 1468 (s), 1445 (s), 1421 (m), 1366 (m), 1124 (w), 787 (m), 735 (s), 706 (s) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): m/z (%) = 333.06, (100) [6Me<sub>3</sub>TPA + H]<sup>+</sup>, 471.95 (40) [{(6Me<sub>3</sub>TPA)Co}<sub>2</sub>(PP)]<sup>2+</sup>, 553.93 (50) [(6Me<sub>3</sub>TPA)Co(PP)]<sup>+</sup>). UV/ Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  ( $\epsilon$ ,  $M^{-1}$  cm<sup>-1</sup>) 330 (20100), 590 (128), 610 (127) nm. Magnetic moment  $\mu_{eff}$  (298 K): 6.35  $\mu_{B}$ .

[(TPA)Co<sup>II</sup>(PPH)](BPh<sub>4</sub>) (4): To a solution of the ligand TPA (0.29 g, 1 mmol) in methanol (5 mL) was added solid cobalt(II) perchlorate hexahydrate (0.36 g, 1 mmol). The orange-red solution was then treated with solid sodium phenylpyruvate (0.18 g, 1 mmol) and the resulting green solution was stirred for a further 5 h at room temperature. After treating the reaction solution with NaBPh<sub>4</sub> (1 mmol), a green solid was isolated. The solid was isolated by filtration, washed with methanol, and dried; yield 0.65 g (78%). C<sub>51</sub>H<sub>45</sub>BCoN<sub>4</sub>O<sub>3</sub> (831.67 g/mol): calcd. C 73.65, H 5.45, N 6.74; found C 73.33, H 4.97, N 6.91. IR (KBr): v = 3429 (m), 3053 (s), 2926 (m), 2854 (m), 1679 (s), 1639 (m), 1608 (s), 1576 (m), 1481 (s), 1439 (m), 1367 (m), 1119, 1103 (m), 767 (m), 735 (s), 708 (s) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): m/z (%) = 349.01 (20) [(TPA)Co]<sup>+</sup>, 511.98 (100) [(TPA)Co(PPH)]<sup>+</sup>. UV/Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  ( $\epsilon$ ,  $M^{-1}$  cm<sup>-1</sup>) 304 (7300), 322 (6600), 452 (475) and 603 (280) nm. Magnetic moment  $\mu_{eff}$  (298 K): 4.17  $\mu_{B}$ .

**[{(6Me<sub>3</sub>TPA)Co<sup>II</sup>}<sub>2</sub>(oxalate)](BPh<sub>4</sub>)<sub>2</sub> (5):** Dry oxygen was bubbled through an acetonitrile solution (10 mL) of complex **3** (0.041 g, 0.026 mmol) for 2 min and the solution was kept under an oxygen atmosphere for 7 h. The solution was concentrated to yield a pink solid. X-ray-quality single crystals were grown from a solvent mixture of dichloromethane and methanol; yield 0.023 g (59%). C<sub>92</sub>H<sub>88</sub>B<sub>2</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>4</sub> (1509.18): calcd. C 73.22, H 5.88, N 7.42; found C 72.31, H 5.76, N 7.33. IR (KBr):  $\tilde{v} = 3051$  (m), 2926 (m), 1655 (s), 1605 (s), 1575 (m), 1446 (m), 787 (m), 737 (s), 706 (s) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *m*/*z* (%) = 435.15 (100) [{(6Me<sub>3</sub>TPA)Co<sub>3</sub>(oxalate)]<sup>2+</sup>, 480.15 (15) [{(6Me<sub>3</sub>TPA)Co-(oxalate)} + H]<sup>+</sup>. UV/Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  (ε, M<sup>-1</sup>cm<sup>-1</sup>) 495 (65), 520 (60), 555 (50) nm. Magnetic moment  $\mu_{eff}$  (298 K): 6.46 μ<sub>B</sub>.

Complex **5** was also prepared independently by reacting the ligand (1 mmol) with cobalt(II) chloride (1 mmol), disodium oxalate (0.5 mmol), and sodium tetraphenylborate in methanol.



**[(TPA)Co<sup>III</sup>(PP)](BPh<sub>4</sub>) (6):** Complex 4 (0.021 g, 0.025 mmol) was dissolved in acetonitrile (5 mL) and dry oxygen was bubbled through the solution for 2 min. The resulting solution was stirred under oxygen for 3 to 4 h during which time the green solution slowly changed to brown. The brown solution was concentrated to obtain a brown solid. Single crystals were isolated upon recrystallization of the solid from a solvent mixture of acetonitrile and methanol; yield 0.017 g (82%).  $C_{51}H_{44}BCoN_4O_3$  (830.66 g/mol): calcd. C 73.74, H 5.34, N 6.74; found C 73.57, H 5.67, N 6.89. IR (KBr):  $\tilde{v} = 3443$  (m), 3051 (s), 2924 (m), 2853 (m), 1643 (s), 1609 (s), 1481 (m), 1446 (m), 1375 (m), 1285 (m), 773 (m), 735 (s), 706 (s) cm<sup>-1</sup>. ESI-MS (in positive ion mode, CH<sub>3</sub>CN): m/z (%) = 349.37 (70) [(TPA)Co]<sup>+</sup>, 511.12 (100) [(TPA)Co(PP)]<sup>+</sup>. UV/Vis in CH<sub>3</sub>CN:  $\lambda_{max}$  ( $\epsilon$ ,  $m^{-1}$  cm<sup>-1</sup>) 322 (22000  $m^{-1}$  cm<sup>-1</sup>), 335 (19000  $m^{-1}$  cm<sup>-1</sup>) nm.

**Reactivity with Dioxygen:** Pure oxygen was bubbled through a solution of the cobalt(II) benzoylformate complex (0.02 mmol) in dry acetonitrile (10 mL) for 2 min. The solution was continuously stirred under oxygen for 7 d. The orange solution was dried to remove the solvent and the residue was treated with 2-M HCl solution. The organic products were then extracted with diethyl ether, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent the solid mass was analyzed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. A control experiment with cobalt(II) perchlorate and sodium benzoylformate in acetonitrile solution under oxygen was performed to elucidate the role of the ligand. No appreciable decomposition of benzoylformate was observed after 7 d.

Ester Derivative of Benzoic Acid: Complex 2 (0.02 mmol) was dissolved in acetonitrile (10 mL) and pure oxygen was passed through the solution for 2 min. Acidic workup of the oxidized solution resulted in a white crude mass which was treated with  $\alpha$ -bromoacetophenone (0.02 mmol) and potassium fluoride (0.04 mmol) in DMF (2 mL). The compound was then isolated according to the reported method and was analyzed by GC–MS.<sup>[41]</sup>

Isolation of Benzaldehyde from the Reaction of 3 with  $O_2$ : Cobalt(II) phenylpyruvate complex 3 was dissolved in dry dichloromethane (10 mL) and oxygen was bubbled through the solution for 2 min. Stirring of the solution was continued for 6 h under oxygen. A saturated solution of  $H_2K_2EDTA$  in water (10 mL) was added and the resulting mixture was stirred overnight. The organic layer was separated and dried with anhydrous  $Na_2SO_4$ . Solvent was removed and the organic product was analyzed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. Benzaldehyde was quantified with respect to the peak assigned for the 6Me<sub>3</sub>TPA ligand.

**Interception Studies:** Cobalt(II) complexes (0.02 mmol) were dissolved in dry acetonitrile (10 mL) and 2,4-di-*tert*-butylphenol or 2,4,6-tri-*tert*-butylphenol (10 equiv.) was added. Oxygen was bubbled through the solution and stirring was continued at room temperature under oxygen for 5 d. The orange solution was dried to remove the solvent and the residue was treated with 2 m HCl solution. The organic products were then extracted with diethyl ether, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was passed through a silica column using diethyl ether as eluent. After removing the solvent the solid mass was analyzed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>.

<sup>1</sup>H NMR spectroscopic data of 4,4',6,6'-tetra-*tert*-butyl-2,2'-biphenol (500 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  = 1.34 (s, 18 H), 1.47 (s, 18 H), 7.13 (d, *J* = 2.5 Hz, 2 H), 7.37 (d, *J* = 2.5 Hz, 2 H) ppm.

<sup>1</sup>H NMR spectroscopic data of 2,6-di-*tert*-butyl-1,4-benzoquinone (500 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  = 1.27–1.28 (br., 18 H), 6.50 (s, 2 H) ppm. Control experiments with cobalt(II) perchlorate and 2,4-di-*tert*-butylphenol or 2,4,6-tri-*tert*-butylphenol in acetonitrile solu-

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tion under oxygen were performed. No appreciable amounts of 4,4',6,6'-tetra-*tert*-butyl-2,2'-biphenol or 2,6-di-*tert*-butyl-1,4-benzoquinone were observed even after 7 d.

Supporting Information (see footnote on the first page of this article): All spectroscopic data for the complexes and crystallographic data for 2,  $3 \cdot CH_2Cl_2$ , 5, and  $6 \cdot 2CH_3CN$  in CIF file format.

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