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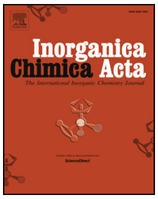

Research paper

A spin-crossover Co(II) complex catalyzes the activation of sp^3 C–H bonds by two-electron oxidants

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ABSTRACT

We recently found that a high-spin Co(II) complex with *N,N*′-dibenzyl-*N,N*′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (bbpc) was capable of catalyzing the oxidation of weak sp^3 C–H bonds by iodosobenzene (PhIO) and *meta*-chloroperbenzoic acid (MCPBA). The bbpc compound could also be oxidized to a Co(III)-peroxo species capable of reacting with aldehydes. The ligand *N*-benzenesulfonyl-*N,N*’-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (bsbpc) reacts with $Co(ClO_4)_2$ to yield a spin-crossover complex, $[Co(bsbpc)(MeCN)_2](ClO_4)_2$. The bsbpc complex catalyzes the oxidation of benzylic and allylic C–H bonds by PhIO and MCPBA to approximately the same extent as the high-spin bbpc compound. The bsbpc complex differs more substantially from the bbpc compound in that it cannot be oxidized to a stable Co(III)-peroxo complex and shows no reactivity with aldehydes.

1. Introduction

Iron complexes have long been explored for their abilities to catalyze the oxidation of C–H bonds by two-electron terminal oxidants, such as H_2O_2 [1]. The C–H activation performed by a variety of non-heme iron oxidants is strongly influenced by the spin-state of the metal center. A series of Fe(IV)-containing complexes with the 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) ligand, $[Fe(O)(TMC)(X)]^{n+}$, was found to activate weak C–H bonds [2]. The rate of these reactions is dependent on the identity of the axial ligand, X, *trans* to the oxo. Faster rates were associated with ligands that allowed better access to the high-spin quintet state. A subsequent study suggested that the inability of low-spin Fe(IV) oxo complexes to activate stronger C–H bonds derives partly from the need to access this more active high-spin state during the reactions [3]. High-spin Fe(IV) oxo species were later characterized and were found to be indeed more reactive and less stable than their low-spin counterparts [4–6]. Spin-state also influences the reactivity of Fe(III)-OOR and Fe(III)-OOH complexes. For the Fe(III)-OOR compounds, the low-spin state favors O–O bond cleavage, whereas the high-spin state promotes scission of the Fe–O bond [7,8]. High-spin Fe(III)-OOH complexes are proposed to react with weak C–H bonds more rapidly than low-spin analogs; the low-spin complexes, however, are better at activating stronger C–H bonds [9].

Non-organometallic cobalt-mediated sp^3 C–H activation, conversely, has been observed only rarely, and most of this has been stoichiometric rather than catalytic with respect to the metal [10–13]. Cobalt is much better known for its ability to catalytically activate sp^3 C–H bonds through organometallic coupling reactions [14–16]. We recently found that a high-spin Co(II) complex with the bulky tetradentate N-donor ligand *N,N*′-dibenzyl-*N,N*′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (bbpc, Scheme 1) could catalyze the oxidation of 9,10-dihydroanthracene, 1,4-cyclohexadiene, and xanthene by iodosobenzene and *meta*-chloroperbenzoic acid [17]. One drawback of the catalyst is that the activity persists for fewer than 30 min. Mass spectrometry of the C–H activation reactions reveals that the bbpc ligand degrades over this time; the methylene bridges between the phenyl groups and the amines appear to be susceptible to oxidation.

In an effort to prolong catalysis, we developed a new organic ligand that contains a sulfonyl linkage in place of the methylene between the metal-coordinating portion of the ligand and the phenyl group: *N*-benzenesulfonyl-*N,N*’-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (bsbpc, Scheme 1). We hypothesized that removing weak and potentially oxidizable benzylic C–H bonds would eliminate pathways for catalyst degradation and thereby extend the reactivity with external substrates. To our mild surprise, we found that the bsbpc ligand yielded a spin-crossover, rather than a high-spin, Co(II) complex. Despite this substantial change to the electronic character of the metal, the compound is still capable of catalyzing C–H activation. The bbpc ligand had also been found to stabilize a Co(III)-peroxo species which was capable of aldehyde deformylation [17]. The bsbpc ligand, conversely, does not support this chemistry.

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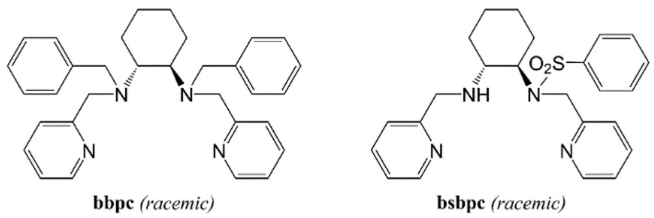

Scheme 1.

2. Experimental section

2.1. Materials

Most chemicals were purchased from Sigma-Aldrich. Acetonitrile (MeCN) and cyclohexanecarboxaldehyde (CCA) were bought from Acros Organics. 2-Phenylpropionaldehyde (2-PPA) and iodosobenzene (PhIO) were obtained from TCI America. All deuterated solvents were purchased from Cambridge Isotopes. Methanol (MeOH) and ethanol (EtOH) were acquired from Pharmaco-Aaper and EMD Chemicals, respectively. H_2O_2 (50% wt) was bought from Fisher Chemical and was calibrated by titration of $KMnO_4$ and H_2SO_4 in water. *N,N'*-Bis(2-pyridylmethyl)-1,2-cyclohexanediamine was prepared through a previously reported procedure [18]. PhIO was kept in a 253 K freezer when not in use. H_2O_2 and MCPBA were kept in a 277 K refrigerator when not in use. Xanthene and 9,10-dihydroanthracene (DHA) were recrystallized twice from EtOH before their use in reactivity assays. CCA was distilled prior to its use.

Caution: Perchlorate salts of metal complexes, peroxides, and peracids are all potentially explosive and should be handled with care. Precautionary measures include working with small quantities and low concentrations of these reagents. Appropriate safety measures, such as protective shields, should be employed during their syntheses and subsequent handling.

2.2. Instrumentation

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on either a 600, 400, or 250 MHz AV Bruker NMR spectrometer. Optical data were collected with a Varian Cary 50 spectrophotometer and were processed and analyzed using software from the WinUV Analysis Suite. IR data were obtained using a Shimadzu IR Prestige-21 FT-IR spectrophotometer. A Thermo Scientific Trace GC Ultra Gas Chromatograph and Thermo Scientific TR-1 and TG-WAXMS columns were used for gas chromatography (GC). A Johnson Matthey magnetic susceptibility balance (model MK I#7967) was used to measure the magnetic moments of solid samples of the metal complexes. Pascal's constants were used to estimate the diamagnetic correction to the susceptibility [19]. High-resolution mass spectrometry (HR-MS) data were collected at the Mass Spectrometer Center at Auburn University on a Bruker microflex LT MALDI-TOF mass spectrometer via direct probe analysis operated in the positive ion mode. Crystalline samples were dried, stored under N_2, and sent to Atlantic Microlabs (Norcross, GA) for elemental analysis.

2.3. Crystallographic Studies

A single crystal of bsbpc was mounted on a glass fiber with Krytox oil and optically aligned on a Bruker APEX Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were performed using an IμSX-ray, a 30 W microfocused sealed tube (MoKα, λ = 0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics. Standard APEX software was used for determination of the unit cell and data collection control. The SAINT software was used for data integration including Lorentz and polarization corrections, and semi-empirical absorption corrections were applied using the program SADABS. The structure for bspbc was solved with the ShelXL software package using direct methods and refined using the Olex2 program. A single crystal of $[Co(bsbpc)(MeCN)_2](ClO_4)$ (1) was mounted on a CryoLoop with Krytox oil and optically aligned on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector. Initial intensity measurements were performed using a PhotonJet source, a 30 W microfocused sealed tube (MoKα, λ = 0.71073 Å) with high-brilliance and high-performance focusing multilayer optics. The diffraction images for **1** were processed and scaled using the CrysAlisPro software. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. The structure was solved with the ShelXT software package and refined using XH software. Selected crystallographic information is listed on Table 1. Atomic coordinates and additional structural information are provided as Supporting Information. The two reported structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC 1834775-1834776).

Table 1
Selected crystallographic data for bsbpc and **1**

Parameter	bsbpc	$[Co(bsbpc)(MeCN)_2](ClO_4)_2 \cdot MeCN$ (**2**)
Formula	$C_{24}H_{28}N_4O_2S$	$C_{30}H_{37}Cl_2CoN_7O_{10}S$
MW	436.58	817.57
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca (#61)*	*P* $(\bar{1})$ *(#2)*
a (Å)	16.5482(16)	10.6448(5)
b (Å)	11.2725(10)	12.2374(6)
c (Å)	23.390(2)	13.2826(6)
a (deg)	90	93.521(4)
b (deg)	90	90.421(4)
g (deg)	90	95.262(4)
V (Å^3)	4363.2(7)	1719.56(14)
Z	8	2
Cryst color	Colorless	Orange
T	180(2)	180(2)
Reflns collected	21798	21604
Unique reflns	3989	7040
R1 (F, I > 2σ(I))	0.0593	0.0448
wR2 (F^2, all data)	0.1139	0.1197

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2.4. Synthesis

N-Benzenesulfonyl-*N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (bsbpc). *N,N'*-Bis(2-pyridylmethyl)-1,2-cyclohexanediamine (0.593 g, 100 mM) and benzenesulfonyl chloride (0.707 g, 100 mM) were dissolved in 20 mL of dry THF under N_2 and stirred for 1 h at room temperature (RT). 20 mL of deionized H_2O was subsequently added, and the organic solvent was removed by rotovaporation. A saturated KOH solution was added dropwise until the pH was above 9; precipitation was observed during the basification. The product was extracted with three portions of CH_2Cl_2. These extracts were combined, dried with Na_2SO_4, and filtered. The CH_2Cl_2 was removed, and the residue was dissolved in a minimal amount of MeCN and cooled in a refrigerator. Slow diffusion of Et_2O into the cooled solution deposited light brownish crystals. Rinsing with cold ether removed the brown color to yield the product as a white crystalline solid (0.646 g, 66%). The crystals were suitable for single crystal X-ray diffraction. ^{1}H NMR ($CDCl_3$, 294 K, 400 MHz): δ 8.48 (1H, d, *J* = 4.84 Hz), 8.20 (1H, d, *J* = 4.24 Hz), 7.77 (2H, q, *J* = 8.75 Hz), 7.54 (4H, m), 7.38 (2H, t, *J* = 7.74 Hz), 7.11 (3H, m), 4.70 (1H, q, *J* = 8.67 Hz), 4.37 (1H, q, *J* = 8.7 Hz), 3.74 (2H, m), 3.25 (1H, q, *J* = 10.99 Hz), 2.42 (1H, s), 2.30 (1H, s), 2.08 (1H, m), 1.61 (2H, s), 1.43 (2H, m), 1.22 (1H, m), 1.08 (2H, quintet, *J* = 10.59 Hz). ^{13}C NMR ($CDCl_3$, 294 K, 100 MHz): 160.59, 157.96, 148.79, 148.74, 140.80, 136.66, 136.30, 132.33, 128.89, 127.20, 123.23, 122.41, 121.553, 121.51, 58.47, 52.24, 32.04, 29.73, 25.59, 24.22. IR (KBr, cm^{-1}): 3448 (w), 3246 (m), 3059 (w),