Dioxygen Activation by a Low-Valent Cobalt Complex Employing a Flexible Tripodal N-Heterocyclic Carbene Ligand

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Abstract: The novel versatile cobalt(I) tris-carbene complex [(TIMEN^{xyl})Co]Cl (**1**) (where TIMEN = (tris[2-(3-arylimidazol-2-ylidene)ethyl]amine) reacts with CO, one-electron oxidizers such as CH$_2$Cl$_2$, and O$_2$ to yield the cobalt complexes [(TIMEN^{xyl})Co(CO)]Cl (**2**), [(TIMEN^{xyl})Co(Cl)]Cl (**3**), and peroxo species [(TIMEN^{xyl})Co(O$_2$)](BPh$_4$) (**5**). All new complexes were fully characterized by ^{1}H NMR, UV/vis, and IR spectroscopy as well as superconducting quantum interference device (SQUID) magnetization measurements and single-crystal X-ray crystallography. The nucleophilic character of the η^2-bound dioxygen ligand in **5** was confirmed by density functional theory (DFT) studies and allows for oxygen-transfer reactions with electron-deficient organic substrates, such as benzoyl chloride.

Introduction

Ligands that enforce a tripodal topology on coordinated metal ions are known to provide powerful platforms for small molecule activation and functionalization. Recently, Schrock and co-workers have developed such a ligand system based on the tris-amidoamine [N$_3$N]$^{3-}$ framework,[1] utilizing it for catalytic dinitrogen reduction.[2] The tetradentate tris-amidoamine tripod creates a protected cavity when coordinated to molybdenum, thereby allowing for isolation and characterization of a variety of intermediates of the reductive dinitrogen cleavage reaction.[2-4] Tripodal ligands have also been shown to stabilize molecular species with unusual reactive terminal functionalities. For example, using an ureayl-derivatized tris-amidoamine chelator, Borovik and co-workers were able to prepare an unprecedented monomeric iron(III) oxo complex.[5] Peters and co-workers have demonstrated that, by employing zwitterionic tris(phosphine)-borate ligands, remarkably reactive late transition metal complexes with terminal imido[6,7] and even nitrido ligands can be synthesized.[8]

Due to the limited accessibility of well-defined polydentate N-heterocyclic carbene (NHC) ligands,[9-16] reports on chelating NHC ligands designed for metal-assisted small-molecule activa-

tion chemistry are rare. Since the isolation of stable imidazol-2-ylidene carbenes in 1991 by Arduengo et al.,[17] N-heterocyclic carbenes have emerged as a predominant ligand class in organometallic coordination chemistry.[18,19] This is mainly due to their successful application in homogeneous catalysis,[20] especially in C—C bond formation[10,21,22] and olefin metathesis reactions.[23,24] We have recently developed a novel nitrogen-anchored tripodal NHC ligand system, TIMEN^R (tris[2-(3-alkylimidazol-2-ylidene)ethyl]amine with R = *tert*-butyl, benzyl), and synthesized the corresponding copper(I)/(II) complexes.[15] The tris-carbene ligand TIMEN binds to transition metals exclusively in a 1:1 fashion and supports controlled reactivity at the metal center.

The xylene-derivatized TIMEN^{xyl} ligand described herein renders the low-valent cobalt(I) tris-carbene complex [(TIMEN^{xyl})Co]Cl (**1**) electronically and structurally flexible for

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additional ligand binding and various redox events such as dioxygen activation. Dioxygen activation at transition metal centers is a fundamentally important process due to its postulated role in biological catalyses.[25-30] Catalytic aerobic oxidation assisted by transition metal complexes therefore remains an attractive, yet challenging, synthetic task.[31-33] There is long-standing interest in the dioxygen chemistry of cobalt complexes owing to their potential use as artificial oxygen carriers[34] and industrial oxidation catalysts.[35-38] The majority of isolated 1:1 cobalt dioxygen adducts feature the oxygen molecule in an end-on (η^1) binding mode and a cobalt center supported by a chelating polyamine ligand.[39-45] Cobalt complexes with side-on (η^2) dioxygen ligands are uncommon.[46-50]
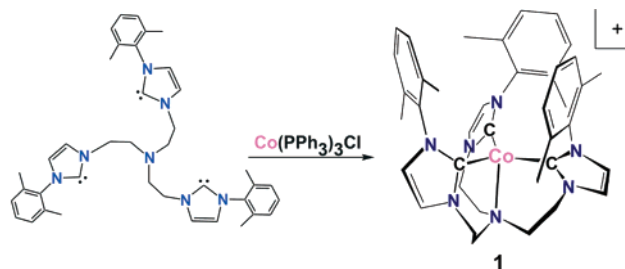
We here report a rare example of a side-on (η^2) peroxo complex with an NHC ligand.[51,52] Density functional theory (DFT) calculations and reactivity studies established the nucleophilic character of the coordinated dioxygen ligand in $[(TIMEN^{xyl})Co(O_2)]^+$. Accordingly, the peroxo complex reacts with strong electrophiles to transfer the O_2 fragment. The reactions of **1** with CO and CH_2Cl_2, yielding the corresponding mononuclear Co(I) carbonyl and Co(II) chloro complexes are also reported.

Results and Discussion

Synthesis of Complex [(TIMEN^{xyl})Co]Cl (1). Following our previously reported method,[13,15] the aryl-substituted tris-

Scheme 1. Synthesis of Complex [(TIMEN^{xyl})Co]Cl (**1**)

carbene ligand tris[2-(3-xylenylimidazol-2-ylidene)ethyl]amine (TIMEN^{xyl}) was prepared by deprotonation of the corresponding imidazolium salt with potassium *tert*-butoxide. Reaction of TIMEN^{xyl} with a suitable cobalt(I) source, i.e., Co(PPh₃)₃Cl, yields the [(TIMEN^{xyl})Co]Cl (**1**) target complex, which precipitates from benzene as an analytically pure yellow powder in ∼80% yield (Scheme 1). Complex **1** possesses saltlike solubility and is only soluble in polar organic solvents such as acetonitrile and DMSO. It is, however, sparsely soluble in tetrahydrofuran (THF) but insoluble in hydrocarbons and diethyl ether.

The ¹H NMR spectrum of **1** in DMSO-d_6 exhibits paramagnetically shifted and broadened peaks and is consistent with the proposed structural formula given in Scheme 1. In this complex, the 3-fold symmetry of TIMEN^{xyl} is preserved, giving rise to 10 distinctive resonances in the range of 75 to −25 ppm. Although the assignment of these signals remains largely equivocal, their positions are diagnostic for determination of the purity and stability of **1** in solution.

Under an inert-gas atmosphere, compound **1** is stable in the solid state but gradually oxidizes to yield the cobalt(II) species [(TIMEN^{xyl})CoCl]Cl (**3**) when stored in acetonitrile or THF solution; replacement of the chloride anion with other counterions does not increase the complexes' stability in solution. This instability in solution greatly hampered our attempt to obtain a crystal structure of **1** in its pure form. In fact, slow ether diffusion into an acetonitrile solution of **1** yielded red, plate-shaped crystals that, according to their NMR spectrum, were a mixture of about 35% **1** and 65% **3**. An X-ray diffraction analysis confirmed cocrystallization of **1** and **3**. The overall structure was modeled and refined with the two cocrystallizing components of **1** (42%) and **3** (58%) (see Figure 1 and Figures S1 and S2 in Supporting Information). In **1**, the TIMEN^{xyl} ligand is tetradentate-coordinated through the three carbenoid carbon
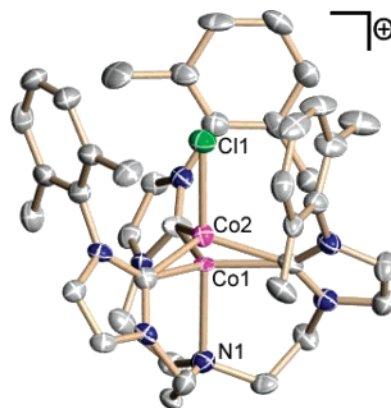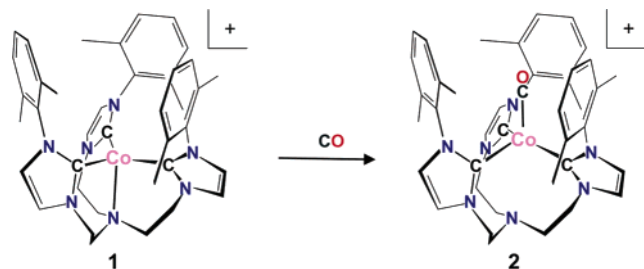
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Figure 1. Overlay representation of the solid-state molecular structures of cocrystallized **1** and **3** (see Figure S2 for independent structures of **1** and **3**).

Scheme 2. Synthesis of Complex [(TIMEN^xyl)Co(CO)]Cl (**2**)

atoms and the anchoring nitrogen atom to the cobalt ion; in **3**, the TIMEN^xyl binds only through the three carbene centers and the axial coordination site of the cobalt ion is occupied by a chloride anion. The cocrystallization of **3** prevents a detailed discussion of the metric parameters of **1**, but the structural data still allow for confirmation of atom connectivities and the cationic structure of **1**. In addition, the structure of **3** deduced from this experiment agrees well with that of an independently synthesized, pure crystal of **3** (vide infra).

Synthesis and Structure of Complex [(TIMEN^xyl)Co(CO)]-Cl (2). In complex **1** the xylene substituents of the functionalized TIMEN^xyl ligand form a well-protected cavity with sufficient access to the cobalt ion for additional ligand binding. To test the reactivity and to further stabilize the electron-rich cobalt(I) ion, complex **1** was reacted with an excess of CO gas (1 atm, Scheme 2). The reaction proceeded smoothly within minutes and the resulting green complex [(TIMEN^xyl)Co(CO)]Cl (**2**) was isolated in 85% yield. The infrared vibrational spectrum of **2** shows an intense absorption band at 1927 cm^{-1}, indicative of a terminal carbonyl ligand.[53] The ^{1}H NMR spectrum of **2** exhibits paramagnetically shifted and broadened resonances between 80 and -15 ppm, suggesting a d^8 high-spin (S = 1) electronic configuration of the Co(I) ion.

The solid-state molecular structure of **2** was determined by X-ray diffraction analysis (Figure 2). The average Co–C$_{carbene}$ distance of 2.039(2) Å is slightly longer than those of other cobalt(I) NHC carbonyl complexes [1.888(3)–1.949(11) Å],[54–56] reflecting a greater degree of steric hindrance, most likely caused by the xylene *o*-methyl groups of the arene substituents. The CO ligand resides on the pseudo-C_3 axis of the [(TIMEN)Co] fragment and is centered within the C_3 propellerlike arrangement of the xylene substituents. The Co–C$_{co}$ and carbonyl C–O bond distances were determined to be 1.8463(19) Å and 1.101(3) Å, respectively. The cobalt center is located +0.392 Å above the idealized trigonal plane defined by the three carbenoid carbon ligands. This, together with an average C$_{carbene}$–Co–C$_{carbene}$
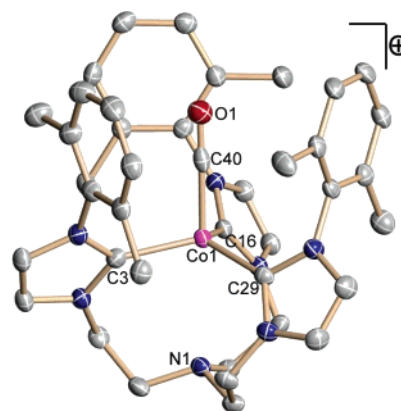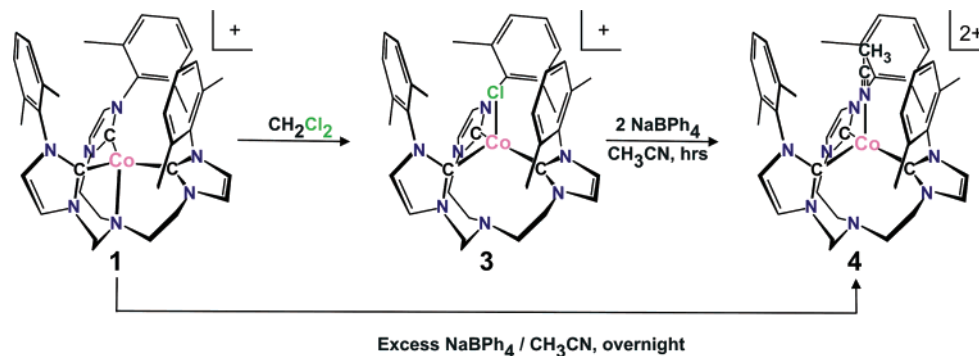

Figure 2. Solid-state molecular structure of [(TIMEN^xyl)Co(CO)]Cl·2CH$_3$CN (**2**·2CH$_3$CN). Hydrogen atoms, anion, and solvent molecules are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (angstroms) and angles (degrees): Co(1)–C(3) 2.0347(17), Co(1)–C(16) 2.0545(17), Co(1)–C(29) 2.0267(16), Co(1)–C(40) 1.8463(19), Co(1)–N(1) 3.034, C(40)–O(1) 1.103(2), C(3)–Co(1)–C(16) 117.92(6), C(3)–Co(1)–C(29) 113.02(6), C(16)–Co(1)–C(29) 118.33(6).

bond angle of 116.42(6)°, suggests that the coordination polyhedron of the cobalt ion in **2** is best described as distorted trigonal pyramidal.

Synthesis and Structure of Complexes [(TIMEN^xyl)Co-(Cl)]Cl (3) and [(TIMEN^xyl)Co(CH$_3$CN)](BPh$_4$)$_2$ (4). On the basis of our observation that, when stored in acetonitrile solution over extended periods of time, **1** slowly oxidizes to form the corresponding cobalt(II) species [(TIMEN^xyl)Co(Cl)]Cl (**3**), we sought to develop an independent synthesis for **3**. Access to **3** was achieved by treatment of **1** with benzyl chloride or chlorinated solvents, such as dichloromethane or chloroform (Scheme 3), yielding blue microcrystals in high yield (>85%). The paramagnetic ^{1}H NMR spectrum of **3** in CD$_2$Cl$_2$ solution shows paramagnetic resonances between 70 and -4 ppm.

Blue crystals suitable for an X-ray diffraction study were obtained by slow ether diffusion into a DMSO solution of **3**. The complex features a four-coordinate cobalt(II) center with a distorted trigonal pyramidal geometry (Figure 3). The TIMEN^xyl ligand coordinates in a tridentate fashion and the axial chloride atom resides inside the pocket provided by the three xylene substituents. The average Co–C distance of 2.077(5) Å and C–Co–C angle of 115.5(2)° are similar to those found in the Co(I) carbonyl complex **2**. In **3**, the displacement of the divalent Co ion from the carbene C_3-plane, however, was found to be +0.448 Å and, thus, is considerably larger than that found in the structure of **2**.

Scheme 3. Synthesis of Complexes [(TIMEN^xyl)Co(Cl)]Cl (**3**) and [(TIMEN^xyl)Co(CH$_3$CN)](BPh$_4$)$_2$ (**4**)
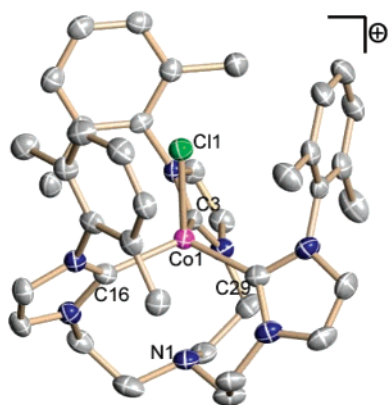
Figure 3. Solid-state molecular structure of [(TIMEN^xyl)Co(Cl)]Cl·DMSO (**3**·DMSO). Hydrogen atoms, anion, and solvent molecules are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (angstroms) and angles (degrees): Co(1)−C(3) 2.078(5), Co(1)−C(16) 2.080(5), Co(1)−C(29) 2.074(5), Co(1)−Cl(1) 2.2557(15), Co(1)−N(1) 3.061, C(3)−Co(1)−C(16) 117.57(19), C(3)−Co(1)−C(29) 114.50(19), C(16)−Co(1)−C(29) 114.4(2).
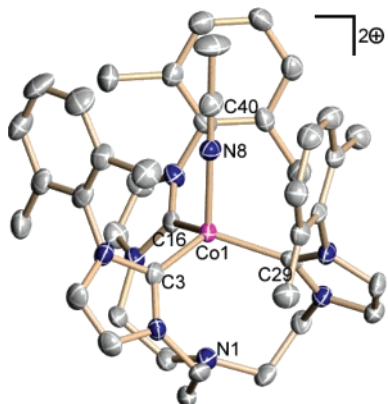

Figure 4. Solid-state molecular structure of [(TIMEN^xyl)Co(CH₃CN)]-(BPh₄)₂·CH₃CN (**4**·CH₃CN). Hydrogen atoms, anions, and solvent molecules are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (angstroms) and angles (degrees): Co(1)−C(3) 2.028(3), Co(1)−C(16) 2.033(3), Co(1)−C(29) 2.047(3), Co(1)−N(8) 2.035(3), Co(1)−N(1) 3.146, C(3)−Co(1)−C(16) 111.71(13), C(3)−Co(1)−C(29) 111.53(13), C(16)−Co(1)−C(29) 121.24(13), Co(1)−N(1)−C(40) 179.1(3).

Chloro complex **3** in acetonitrile reacts with NaBPh₄ to yield the dicationic acetonitrile complex [(TIMEN^xyl)Co(CH₃CN)]-(BPh₄)₂ (**4**) (Scheme 3) and NaCl precipitation. After filtration of the blue solution and storage at low temperatures, dark-blue plate-shaped crystals of **4** were isolated in 80% yield. Alternatively, an acetonitrile solution of **1** containing NaBPh₄ will also yield **4** within a few days. The ¹H NMR spectrum of **4** exhibits paramagnetically shifted and broadened signals spread over a wider range (100 and −8 ppm) compared to complex **3**.

The molecular structure of **4** displays features similar to those of **2** and **3**, namely, a four-coordinate cobalt ion and a tris-chelating TIMEN^xyl ligand with distorted trigonal pyramidal coordination geometry (Figure 4). The average Co−C distance is 2.036(3) Å and the C−Co−C angle is 114.83(13)°. The axial
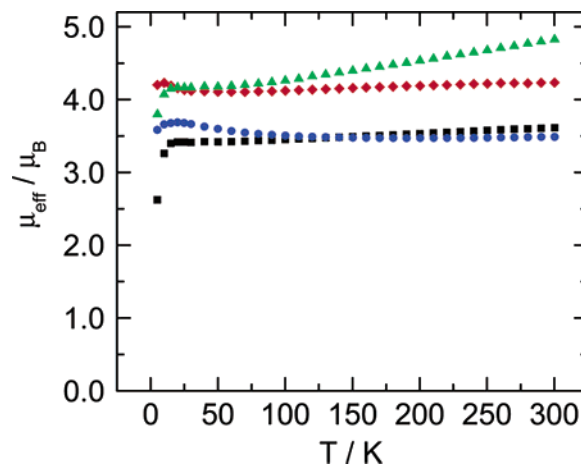
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Figure 5. Plots of the effective magnetic moments, μ_{eff}, versus temperature from temperature-dependent SQUID magnetization measurements for complexes **1** (black ■), **2** (blue ●), **3** (red ◆), and **4** (green ▲).
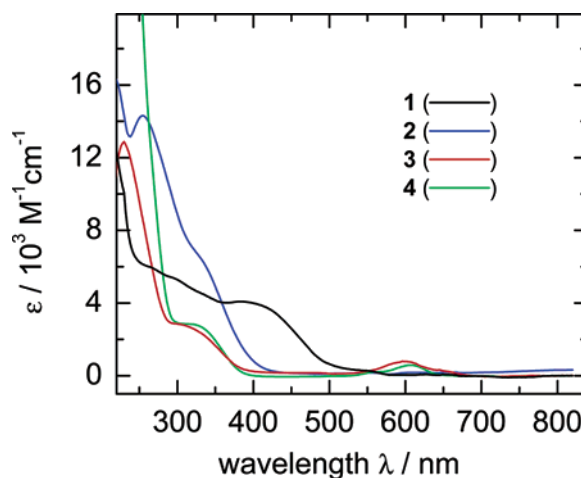

Figure 6. UV/vis absorption spectra of complexes **1**−**4** recorded in acetonitrile solutions.

acetonitrile molecule is essentially linearly coordinated, with a Co−N−C angle of 179.1(3)°. The displacement of the Co(II) ion from the trigonal plane of the carbene carbon ligands was determined to be +0.469 Å and, thus, is very similar to that found in **3**.

Electronic Absorption Spectra and Magnetic Properties of Complexes 1−4. Paramagnetic complexes **1**−**4** were characterized by SQUID magnetization measurements and electronic absorption spectroscopy (Figures 5 and 6).

At room temperature, cobalt(I) complexes **1** and **2** exhibit magnetic moments of $3.65\mu_B$ and $3.49\mu_B$, respectively. These values are comparable to that of $3.8\mu_B$ reported for a related cobalt(I) complex [(Tp)Co(C₂H₄)][57] and exceed the calculated spin-only value of $2.83\mu_B$ for a high-spin d⁸ ($S = 1$) system. Such deviation is generally considered to be caused by a substantial orbital angular momentum contribution from the cobalt ion. In the temperature range between 300 and 15 K, the magnetic moment of **1** is nearly constant at $3.65\mu_B$, but, likely due to zero-field splitting, decreases rapidly below 15 K until reaching a minimum of $2.60\mu_B$ at 5 K. In comparison, the magnetic moment of **2** shows little variation over the entire temperature range from 300 to 5 K.

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Table 1

complex	absorption maxima λ_{max}/nm (molar extinction coefficient ϵ/cm^{-1} M^{-1})
1	220 (12426), 252 (6200), 384 (4080)
2	220 (16274), 254 (14300), 332 (6830)
3	220 (11262), 230 (12880), 308 (2890), 596 (782)
4	220 (78706), 324 (2801), 558 (201), 606 (581)

Scheme 4. Synthesis of Peroxo Complex [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ (**5**)
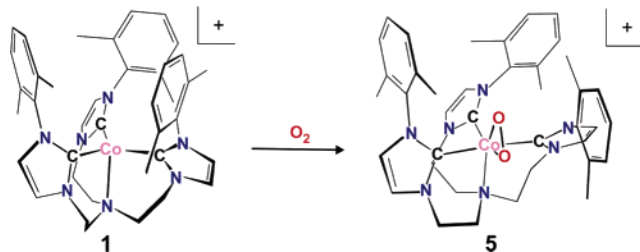
Cobalt(II) complexes **3** and **4** exhibit magnetic properties characteristic for an ion with 3d^7 high-spin ($S = ^3/_2$) electron configuration:[58] Complex **3** exhibits a temperature-independent magnetic moment of 4.23μ_B in the temperature range between 300 and 5 K. The magnetic moment of complex **4**, on the other hand, has a room-temperature value of 4.83μ_B, which decreases gradually with decreasing temperature until it plateaus between 60 and 15 K. The magnetic moment decreases again at 10 K, reaching a minimum value of 3.80μ_B at 5 K. The room-temperature moments of both complexes **3** and **4** fall in the range between 4.3μ_B and 4.8μ_B. This range is typically observed for high-spin cobalt(II) complexes with pseudo-tetrahedral or lower symmetry[58−61] and is suggestive of a quartet magnetic ground state for complexes **3** and **4**.

Figure 6 and Table 1 summarize the UV/vis spectral data for complexes **1**−**4**. All absorption spectra are dominated by intense charge-transfer bands in the UV and near-visible regions. The visible spectra of cobalt(II) complexes **3** and **4** show d−d transitions at around 600 nm (ϵ = 782 and 581 M^{-1} cm^{-1}), characteristic for high-spin Co(II) complexes in a distorted ligand field.[59] The positions and intensities of these bands correlate well with their distorted trigonal pyramidal geometry (pseudo-C_{3v}).

Synthesis and Structure of the Cobalt Dioxygen Complex [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ (5). The unusual molecular and electronic structure of the coordinatively unsaturated complex **1** prompted us to investigate its reactivity toward dioxygen. We found that a solution of **1** reacts cleanly with dioxygen at room temperature to form a 1:1 cobalt dioxygen adduct [(TIMEN^{xyl})-Co(O$_2$)]$^+$ (Scheme 4). When the reaction is carried out in THF and in the presence of 1 equiv of NaBPh$_4$, the resulting complex [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ (**5**) precipitates from the reaction mixture and is isolated as an analytically pure pale pink powder.

On the basis of the O−O stretching frequency, dioxygen complexes are generally classified as either peroxo (930−740
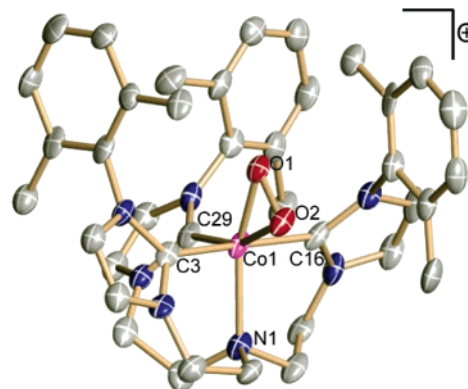
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Figure 7. Solid-state molecular structure of complex [(TIMEN^{xyl})Co(O$_2$)]-BPh$_4$·Et$_2$O (**5**·Et$_2$O). Hydrogen atoms, anion, and solvent molecules are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (angstroms) and angles (degrees): Co(1)−C(3) 2.003(4), Co(1)−C(16) 1.934(4), Co(1)−C(29) 1.950(4), Co(1)−N(8) 2.137(3), Co(1)−O(1) 1.855(2), Co(1)−O(2) 1.906(2), O(1)−O(2) 1.429(3), C(3)−Co(1)−C(16) 169.67(14), C(3)−Co(1)−C(29) 98.65(14), C(16)−Co(1)−C(29) 91.56(14), O(1)−Co(1)−O(2) 44.64(10), N(1)−Co(1)−C(3) 89.64(13), N(1)−Co(1)−C(16) 91.56(14), N(1)−Co(1)−C(29) 89.27(13).

cm^{-1}) or superoxo (1200−1070 cm^{-1}) species.[62] In the infrared vibrational spectrum of **5**, the O−O stretching frequency ν_{O-O} is found at 890 cm^{-1}, and it shifts to 840 cm^{-1} in the corresponding ^{18}O-labeled compound [(TIMEN^{xyl})Co(^{18}O$_2$)]BPh$_4$. The isotopic shift of 50 cm^{-1} agrees well with the 51 cm^{-1} calculated from a simple diatomic harmonic oscillator model. Accordingly, the infrared spectra of **5** suggest the formation of a side-on peroxo complex.

The ^{1}H and ^{13}C NMR spectra of **5** are consistent with a diamagnetic cobalt(III) peroxo species. In the ^{13}C NMR spectrum, signals from the carbenoid carbons are not observed, probably due to coupling with the cobalt ion ($I = ^7/_2$, 100%). Both ^{1}H and ^{13}C spectra, however, indicate a 3-fold symmetry in the coordinated TIMEN^{xyl} ligand, suggesting a fluxional behavior of **5** in solution. The UV/vis absorption spectrum of **5** exhibits two weak d−d transitions centered at 484 (ϵ = 100 cm^{-1} M^{-1}) and 646 nm (ϵ = 35 cm^{-1} M^{-1}) (see Figure S3, Supporting Information). The low extinction coefficients are consistent with the pseudo-octahedral geometry of the complex (vide infra).

The molecular structure of **5** was established by X-ray crystallography (Figure 7). The hexacoordinate cobalt ion is situated in the plane defined by the two oxygen atoms of the dioxygen ligand, the nitrogen atom on the nexus of the TIMEN framework, and one carbene carbon from the TIMEN^{xyl} ligand, thereby bisecting the tetradentate chelator. The pseudo-octahedral coordination sphere is completed by the remaining two carbene carbon pendant arms of TIMEN^{xyl} in the axial positions. The dioxygen ligand coordinates side-on with an O−O distance of 1.429(3) Å. This O−O bond distance falls well within the range of typical peroxide complexes (1.4−1.5 Å)[63] and is comparable with other rare cobalt(III) peroxo complexes [1.414(12)−1.441(11) Å].[46−49] This distance differs substantially, however, from the cobalt dioxygen complex [Tp′Co(O$_2$)] with the structurally related hydro tris(pyrazolyl)borate sup-

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porting ligand [1.355(3) Å at $T = -123$ °C and 1.262(8) Å at room temperature].[50,63] It is noteworthy that the structurally determined O—O bond distance correlates well with the observed O—O stretching frequency.[63] The Co—O bonds are slightly asymmetric with bond distances of 1.855(2) and 1.906(2) Å. With an average value of 1.962(4) Å, the Co—C distances are shorter than those of complexes **2**–**4**, reflecting the smaller radius of the cobalt(III) ion. In **5**, two C—Co—C angles were found to be close to 90° and a third C—Co—C angle was close to 180° [C3—Co1—C29 = 98.65(14), C16—Co1—C29 = 91.63(15), and C3—Co1—C16 = 169.67(14)]. This, together with an average N—Co—C angle of 90.2(1)°, demonstrates the remarkable flexibility of the TIMEN ligand system, stabilizing complexes with trigonal planar, trigonal pyramidal, and octahedral coordination geometries.

Complex **5** represents a rare example of a metal NHC complex with a coordinating dioxygen ligand.[52] The ability of TIMEN^{xyl} to stabilize a monomeric cobalt peroxo entity likely arises from several factors: the tetradentate chelator is strongly electron-donating and, thus, is able to accommodate the high-valent Co(III) ion; the ligand backbone is very flexible and enables TIMEN^{xyl} to form octahedral complexes; and the three xylene substituents flank the activated dioxygen ligand, thereby effectively blocking the commonly observed bimolecular decomposition pathway to form μ-peroxo dimers.

DFT Study on Complex [(TIMEN^{xyl})Co(O$_2$)]$^+$. DFT calculations were carried out on the cationic part of the high-valent peroxo complex **5**. The calculation resulted in a geometry that is in good agreement with the experimentally determined one. The calculated O—O distance of 1.432 Å is very close to that of 1.429(3) Å found in the solid-state molecular structure of **5**, and the Co—O distances of 1.852 and 1.905 Å are almost identical to the experimental values of 1.855(2) and 1.906(2) Å. The calculated Co—C and Co—N distances with 1.974 and 2.172 Å are also comparable to their experimental counterparts [1.962(4) and 2.137(3) Å].

Inspection of the frontier orbitals of complex **5** confirms that the complex's diamagnetism originates from a d^6 low-spin ($S = 0$) cobalt(III) center with a dative peroxo ligand (Figure 8). The highest occupied molecular orbital (HOMO) is predominantly composed of dioxygen π^* orbitals with some minor contribution from the metal d orbital. Five nearby orbitals, namely, lowest unoccupied molecular orbital (LUMO) + 1, LUMO, HOMO − 1, HOMO − 2, and HOMO − 3, are mainly metal d-orbital-based. The shapes and relative positions of these orbitals indicate that the cobalt ion has a $d_{xy}^2 d_{xz}^2 d_{yz}^2 d_{z^2}^0 d_{x^2-y^2}^0$ electronic configuration. The presence of a high-lying, filled dioxygen π^* orbital suggests the coordinated dioxygen ligand to be nucleophilic.

Reactivity of [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ (5). Transition metal peroxo complexes are classified as either nucleophilic or electrophilic according to their reactivity with organic substrates.[31,64−66] While reaction of triphenylphosphine to give triphenylphosphineoxide is used to assess metal peroxides' electrophilicity,[67] the nucleophilicity of peroxo species is
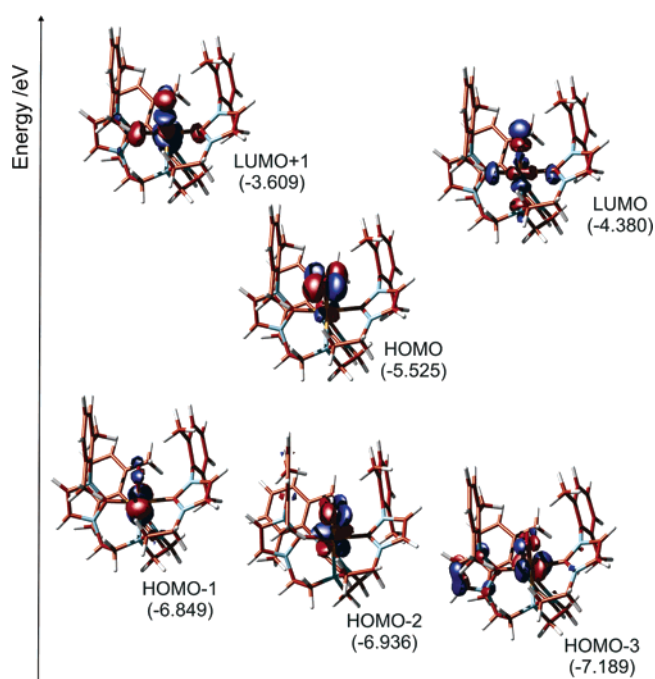

Figure 8. Energies and relative positions of the frontier molecular orbitals of [(TIMEN^{xyl})Co(O$_2$)]$^+$. Calculations are performed at the BP86/ZORA/TZP level with the ADF 2003.01 program suites.

assessed by reaction with the extremely electron-deficient olefin tetracyanoethylene (TCNE).[68] While early transition metal peroxides, such as [(porphyrin)Ti(O$_2$)],[67] reportedly react as electrophiles, late transition metal peroxides, like [(PPh$_3$)$_2$Pt(O$_2$)][68] and [(porphyrin)Fe(O$_2$)]$^-$,[67,69] generally are nucleophilic. As suggested by the DFT study, peroxo complex **5** is nucleophilic and, accordingly, only reacts with electron-deficient organic substrates.

An acetonitrile solution of complex **5** reacts with benzoyl chlorides, for instance, yielding complex **4** and phenyl benzoate quantitatively. The NMR and absorption spectra of **4** isolated from this reaction are identical to those of an independently synthesized sample prepared as described above. The only tractable organic product identified in this reaction was phenyl benzoate, identified by NMR, IR, and gas chromatography−mass spectrometry (GC-MS). A possible reaction mechanism is shown in Scheme 5. In a first step, the coordinated dioxygen attacks benzoyl chloride to form a cobalt(III) peroxyphenyl acetate [(TIMEN)CoOOC(O)Ph]$^{2+}$,[70] which undergoes homolytic Co—O bond cleavage[31] to give a cobalt(II) species and a •OOC(O)Ph radical. The organic radical then decomposes into CO$_2$ and a •OPh radical, which in turn reacts with another molecule of benzoyl chloride to form the final PhOC(O)Ph product.[71] In support of this mechanism, we find that Ph^{18}OC(O)Ph is produced when an ^{18}O$_2$-labeled sample of **5** is employed in the reaction. Unfortunately, we are unable to detect any CO$_2$ evolution from the reaction mixture. This is likely due to the small, stoichiometric quantities of CO$_2$ released in this reaction.

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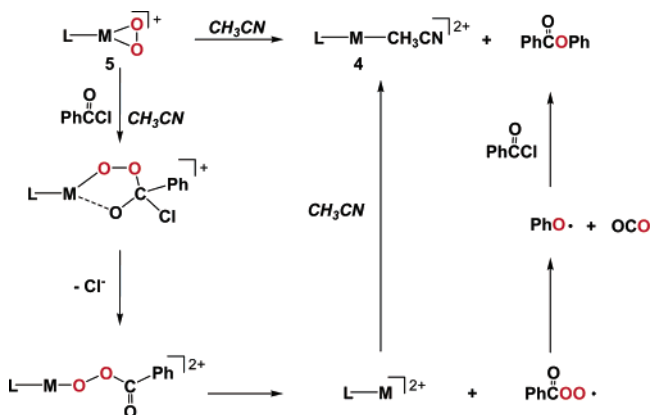(71) The fate of the chlorine radical generated in this reaction is not clear. Formation of Co(II)-Cl species was not observed.

Scheme 5. Proposed Mechanism for the Reaction of **5** with Benzoyl Chloride

Complex **5** also reacts with electron-deficient alkenes. Reaction of **5** with benzylidenemalonitrile yields **4** and benzyl aldehyde, and reaction of **5** with TCNE yields **4** and unidentified organic compounds. The mechanisms of these reactions are currently under investigation, but on the basis of the reaction products, we suspect homolytic Co−O bond cleavage as part of the mechanism. Palladium and platinum peroxo complexes undergo similar reactions via a 2 + 2 cycloaddition pathway to give cyclic peroxy adducts.[68,72]

We also treated **5** with α,β-unsaturated alkenes such as 2-cyclohexene-1-one, 1,4-naphthoquinone, and 2-methyl-1,4-naphthoquinone, but no reaction was observed during an extended period of time. Likewise, complex **5** also is inert toward styrene, cyclohexene, and triphenylphosphine, confirming its lack of electrophilicity.

Valentine and co-workers have classified peroxo species into class I and II nucleophiles according to their relative nucleophilicity.[67] Class I nucleophiles react not only with highly electron-deficient substrates such as TCNE and acyl halide but also with enones and quinones. Class II nucleophiles, on the other hand, merely react with TCNE and acyl halides. Accordingly, the reactivity of complex **5** identifies it as class II nucleophile. Other class II nucleophiles include group VIII metal peroxides, such as $[(PPh_3)_2Pd(O_2)]$, $[(PPh_3)_2Pt(O_2)]$, and $[(PPh_3)_2Ir(CO)(O_2)]I$.[68,72,73]

Comparison of the Tris-Carbene TIMEN and Analogous Tris-Phosphine Ligand Systems. The unique electronic properties of NHCs render the N-anchored tris-carbene TIMEN ligand system considerably diverse from known analogous polydentate phosphine chelators,[74] such as the neutral NP_3 (P = PPh_2) ligand by Sacconi[75−78] and the anionic $PhBP_3^-$ system (P = PPh_2, P^iPr_2) developed by Peters et al.[6−8,60,79] These differences are reflected in the coordination polyhedra and electronic properties of the isolated Co-TIMEN complexes **1−4**. While, with cobalt(I) for instance, the TIMEN ligand system

forms the high-spin carbonyl species $[(TIMEN)Co(CO)]^+$, phosphine-based ligand systems NP_3 and $PhBP_3^-$ (P = PPh_2) form diamagnetic complexes $[(NP_3)Co(CO)]^+$ and $[(PhBP_3)-Co(CO)_2]$, respectively. The cobalt(II) halide $[(TIMEN^{xyl})-CoCl]^+$ is four-coordinate, distorted trigonal pyramidal, and high-spin; the equivalent phosphine species $[(NP_3)CoCl]^+$, however, is five-coordinate, trigonal-bipyramidal, and high-spin;[75] $[(PhBP_3)CoI]$ is four-coordinate, pseudo-tetrahedral, and low-spin.[60]

The steric properties of the TIMEN ligand system are also unique and are generally beneficial for the stabilization of reactive intermediates. While the sterics of coordinated polyphosphine ligands are regulated by substituents on the coordinating phosphorus atom, the sterics of TIMEN are controlled by substituents at the imidazole N3 position. Upon formation of (distorted) tetrahedral metal phosphine complexes, the substituents all point away from the metal center. As a result, the axial binding site in these complexes is exposed and dimeric compounds form readily via binuclear decomposition pathways. Even the sterically encumbering and versatile $PhB(^iPr_2P)_3^-$ ligand system does not prevent such dimerization as evidenced by a unique but highly reactive terminal iron(IV) nitrido complex $[(PhB(^iPr_2P)_3)Fe\equiv N]$ that forms a dinitrogen-bridged dinuclear ferrous species.[8] Due to constrains of the sp^2-hybridized ring nitrogen, aryl substituents in complexes of the $TIMEN^R$ ligand are oriented perpendicular to the trigonal tris-carbene metal plane, thereby forming a deep, well-protected binding cavity. As a result, in complexes of the type $[(TIMEN)M(L_{ax})]^{n+}$, binuclear decomposition pathways are effectively suppressed.

This steric difference is similarly evident for TIMEN and β-diketiminate ligand systems.[80−85] It was reported that the cobalt(I) complex of the xylene-functionalized β-diketiminate ligand, namely, $[(Me_2NN)Co(\eta^6$-toluene)] $(Me_2NN = 2,4$-bis(2,6-dimethylphenyllimido)pentane), reacts with dioxygen to form a dinuclear $[(Me_2NN)Co(\mu-O)_2Co(NNMe_2)]$ complex. Monomeric dioxygen adducts could not be isolated from this reaction.[85] The differences in dioxygen reactivity of $[(Me_2NN)-Co(\eta^6$-toluene)] and $[(TIMEN^{xyl})Co]^+$ may thus also be steric in origin.

Conclusion

The low-valent and coordinatively unsaturated cobalt(I) tris-carbene complex $[(TIMEN^{xyl})Co]Cl$ (**1**) has been synthesized and characterized. This versatile starting material reacts with CO, CH_2Cl_2, and O_2 to yield the cobalt carbonyl $[(TIMEN^{xyl})-Co(CO)]Cl$ (**2**), the chloro $[(TIMEN^{xyl})Co(Cl)]Cl$ (**3**), and peroxo $[(TIMEN^{xyl})Co(O_2)](BPh_4)$ (**5**) complexes. Spectroscopic and structural characterization of all complexes **1−5** (including the acetonitrile complex $[(TIMEN^{xyl})Co(NCCH_3)](BPh_4)_2$ (**4**)) has allowed important insights into structure/reactivity relations. The X-ray analyses revealed the remarkable flexibility of the tripodal ligand system TIMEN, stabilizing distorted trigonal pyramidal,

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four-coordinate cobalt(I) and cobalt(II) complexes as well as a six-coordinate cobalt(III) complex with pseudo-octahedral geometry. This structural flexibility, allowing formation of a large variety of 1:1 metal complexes,[15] is provided by the anchoring nitrogen atom of the carbene tripod. We have demonstrated that this nitrogen atom additionally holds potential to serve as a two-electron σ-donor ligand to aid stabilization of higher valent complexes such as the cobalt(III) peroxo complex reported here. The stability of the monomeric cobalt(III) peroxo complex [(TIMEN^{xyl})Co(O$_2$)](BPh$_4$) is increased by steric protection of the bulky xylene substituents on the TIMEN imidazole rings. The sterically well-protected coordinated dioxygen ligand reacts with electron-deficient organic substrates. This experimentally determined dioxygen reactivity correlates well with the theoretically predicted reactivity as established by DFT calculations. One-electron reduction of complex **5** is expected to further increase the nucleophilicity of the dioxygen ligand.

The ability of the polydentate carbene ligand TIMEN^R (R = aryl) to stabilize both low- and high-valent metal ions and its unique steric properties suggest that the [(TIMEN^R)M] scaffold is well-suited for hosting other highly reactive terminal functionalities, e.g., monodentate imido, nitrido, and oxo ligands. Efforts in pursuing such species are currently underway.

Experimental Section

Methods and Procedures. Manipulations of air-sensitive compounds were performed under a dry nitrogen atmosphere by standard Schlenk techniques and inert-gas gloveboxes (MBraun Labmaster by M. Braun, Inc.). Solvents were purified on a two-column solid-state purification system (Glasscontour Systems, Joerg Meyer, Irvine, CA) and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over nitrogen and activated molecular sieves prior to use. All NMR spectra were recorded on Varian spectrometers operating at 400/300 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) at room temperature (20 °C) in benzene-d_6, acetonitrile-d_3, dichloromethane-d_2, and DMSO-d_6 solutions, respectively. The signals were referenced to residual solvent peaks unless noted otherwise (δ in parts per million, ppm). Solid-state magnetization measurements of powdered samples were recorded on a SQUID magnetometer (Quantum Design) at 10 kOe between 5 and 300 K. Magnetic susceptibility data were corrected for background and underlying diamagnetic contributions by use of tabulated Pascal constants.[86] Data reproducibility was carefully checked in multiple individual measurements of independently synthesized samples. Infrared spectra (400–4000 cm^{-1}) of solid samples were obtained on a Thermo Nicolet Avatar 360 Fourier transform infrared (FT-IR) spectrometer as KBr pellets. Electronic absorption spectra were recorded from 190 to 820 nm (HP 8452A diode-array UV/vis spectrophotometer). Elemental analyses were performed by Kolbe Microanalytical Laboratory (Mülheim a.d. Ruhr, Germany).

Computational Details. DFT calculations on complex **5** were carried out with the Amsterdam Density Functional program package ADF, release 2003.01.[87] The Vosko, Wilk, and Nusair (VWN) local density approximation,[88] Becke's exchange correlation,[89] and Perdew correlation[90] were used. The calculation also included scalar relativistic effects (ZORA)[91] for all atoms. Uncontracted Slater-type orbitals (STOs)[92] were used as basis functions. Co: triple-ζ basis set augmented with a set of p functions and frozen core 2p. N: triple-ζ basis set augmented with

a set of d functions and frozen core 1s. C: triple ζ-basis set augmented with a set of d functions and frozen core 1s. O: triple ζ-basis set augmented with a set of d functions and frozen core 1s. H: triple-ζ basis set augmented with a set of p functions. This basis combination is denoted TZP in the ADF program. No symmetry was specified in the calculations starting from X-ray defined geometry of the cationic portion of **5**; the counteranion was not included in the calculation.

Molecular orbitals were visualized by use of the MOLDEN program package (http://www.cmbi.kun.nl/~schaft/molden/molden.html). ADFrom program was used to convert the TAPE21 file from ADF into a MOLDEN file.

Starting Materials. Tris(2-chloroethyl)-amine and 1-(2,6-xylyl)-imidazole were prepared following literature procedures.[93,94] Chloro-tristriphenylphosphine cobalt(I) (Aldrich), tetracyanoethylene (Aldrich), benzylidenemalonitrile (Aldrich), benzoyl chloride (Fischer), sodium tetraphenylborate (Acros), and potassium *tert*-butoxide (Acros) were obtained from commercial sources and used as received. Carbon monoxide and dioxygen gases were purchased from Matheson Tri-gas, and 95% ^{18}O-labeled O$_2$ was ordered from Cambridge Isotope Laboratories, Inc. The imidazolium salt [H$_3$TIMEN^{xyl}](PF$_6$)$_3$ and free carbene TIMEN^{xyl} were prepared by modifying the previously described methods.[15]

Synthesis: [H$_3$TIMEN^{xyl}](PF$_6$)$_3$. A 50 mL flask was charged with tris(2-chloroethyl)amine (1.58 g, 7.7 mmol) and 1-(2,6-xylyl)imidazole (4.00 g, 60 mmol), and the mixture was heated to 150 °C for 2 days. During this time, a brown solid precipitated from the solution. The solid was filtered off and dissolved in 20 mL of methanol; this solution was filtered and then evaporated to dryness to yield the crude product [H$_3$TIMEN^{xyl}]Cl$_3$. The hygroscopic chloride salt was converted to the corresponding, stable hexafluorophosphate salt, [H$_3$TIMEN^{xyl}](PF$_6$)$_3$, by addition of a solution of NaPF$_6$ (3.88 g, 23.1 mmol) in 20 mL of methanol. The white hexafluorophosphate salt precipitated immediately and was collected by filtration, washed with small volumes of cold methanol, redissolved in acetone, and filtered. The solvent was evaporated to dryness and the resulting solid was dried in a vacuum (6.5 g; yield 80%).

^{1}H NMR (300 MHz, DMSO-d_6, 20 °C): δ 9.46 (s, 3H), 8.09 [d, ^3J(H,H) = 1.1 Hz, 3H], 8.02 [d, ^3J(H,H) = 1.1 Hz, 3H], 7.49 [t, ^3J(H,H) = 7.8 Hz, 3H], 7.39 [d, ^3J(H,H) = 7.8 Hz, 6H], 4.48 [t, ^3J(H,H) = 6.0 Hz, 6H], 3.26 (s, 9H), and 2.12 ppm (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C): δ 137.3, 136.6, 133.5, 130.6, 128.7, 123.6, 123.4, 52.2, 46.9, and 17.0 ppm.

[TIMEN^{xyl}]. A solution of potassium *tert*-butoxide (0.428 g, 3.81 mmol) in THF was added dropwise to a suspension of [H$_3$TIMEN^{xyl}]-(PF$_6$)$_3$ (1.00 g, 0.95 mmol) in 5 mL of THF and stirred for 1 h. The solution was then evaporated to dryness and the solid residue was dissolved in 15 mL of diethyl ether. The resulting solution was filtered and the filtrate was evaporated to dryness in a vacuum. The solid was collected, washed with cold pentane, and dried in a vacuum (0.43 g; yield 75%).

^{1}H NMR (300 MHz, DMSO-d_6, 20 °C): δ 7.32 [d, ^3J(H,H) = 1.1 Hz, 3H], 7.21 (m, 3H), 7.14 (m, 6H), 7.06 [d, ^3J(H,H) = 1.1 Hz, 3H], 4.08 [t, ^3J(H,H) = 6.0 Hz, 6H], 3.01 [t, J(H,H) = 6.0 Hz, 6H], and 1.94 ppm (s, 18H). ^{13}C NMR (100 MHz, benzene-d_6, 20 °C): δ 211.8, 141.4, 135.8, 121.3, 120.5, 120.3, 119.9, 119.6, 67.5, 56.6, 49.7, 32.2, and 18.4 ppm.

[(TIMEN^{xyl})Co]Cl (1). A solution of (PPh$_3$)$_3$CoCl (1.1 g, 1.24 mmol) in 5 mL of benzene was added dropwise to a solution of TIMEN^{xyl} (0.76 g, 1.24 mmol) in 5 mL of benzene. The reaction mixture was allowed to stir for 1 h, during which a yellow-brown precipitate formed.

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The precipitate was filtered, washed with benzene and diethyl ether, and dried in a vacuum (0.69 g; yield 79%).

^{1}H NMR (300 MHz, DMSO-d_6, 20 °C): δ 72.1 (s, 3H, $\Delta\nu_{1/2}$ = 62 Hz), 27.3 (s, 3H, $\Delta\nu_{1/2}$ = 51 Hz), 15.5 (s, 3H, $\Delta\nu_{1/2}$ = 46 Hz), 7.8 (s, 9H, $\Delta\nu_{1/2}$ = 81 Hz), 7.0 (s, 6H, $\Delta\nu_{1/2}$ = 37 Hz), 5.5 (s, 3H, $\Delta\nu_{1/2}$ = 30 Hz), 4.4 (s, 3H, $\Delta\nu_{1/2}$ = 32 Hz), −2.8 (s, 3H, $\Delta\nu_{1/2}$ = 18 Hz), −5.0 (s, 9H, $\Delta\nu_{1/2}$ = 93 Hz), and −24.0 ppm (s, 3H, $\Delta\nu_{1/2}$ = 20 Hz). Elemental analysis (%) calcd for $C_{39}H_{45}N_7CoCl$: C 66.33, H 6.42, N 13.88. Found: C 66.09, H 6.22, N 13.57.

[(TIMEN^{xyl})Co(CO)]Cl (2). A yellow solution of [(TIMEN^{xyl})-Co]Cl (30 mg, 0.04 mmol) in acetonitrile was sparged with carbon monoxide gas, resulting in an immediate color change to green. The reaction mixture was stirred for 30 min, filtered through Celite, and evaporated to give **2** as a green solid. The precipitate was collected by filtration, washed with diethyl ether, and dried in a vacuum (25 mg; yield 85%). Green crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a saturated acetonitrile solution of **2** at room temperature.

^{1}H NMR (300 MHz, acetonitrile-d_3, 20 °C): δ 76.0 (s, 3H, $\Delta\nu_{1/2}$ = 15 Hz), 36.1 (s, 3H, $\Delta\nu_{1/2}$ = 53 Hz), 25.7 (s, 3H, $\Delta\nu_{1/2}$ = 11 Hz), 11.7 (s, 3H, $\Delta\nu_{1/2}$ = 17 Hz), 10.1 (s, 3H, $\Delta\nu_{1/2}$ = 15 Hz), 5.8 (s, 3H, $\Delta\nu_{1/2}$ = 29 Hz), 3.9 (s, 3H, $\Delta\nu_{1/2}$ = 37 Hz), 1.4 (s, 9H, $\Delta\nu_{1/2}$ = 49 Hz), −3.4 (s, 3H, $\Delta\nu_{1/2}$ = 39 Hz), and −10.7 ppm (s, 9H, $\Delta\nu_{1/2}$ = 106 Hz). IR (KBr): ν(CO) = 1927 cm^{-1}. Elemental analysis (%) calcd for $C_{40}H_{45}N_7OCoCl$: C 65.43, H 6.17, N 13.35. Found: C 65.37, H 5.96, N 13.28.

[(TIMEN^{xyl})CoCl]Cl (3). [(TIMEN^{xyl})Co]Cl (50 mg, 0.71 mmol) was dissolved in 2 mL of dichloromethane to form a blue solution. Diethyl ether was then diffused into the solution at room temperature to give blue crystals of **3** overnight. The crystals were collected by filtration, washed with diethyl ether, and dried in a vacuum (46 mg; yield 87%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a solution of **3** in DMSO at room temperature.

^{1}H NMR (300 MHz, dichloromethane-d_2, 20 °C): δ 67.4 (s, 3H, $\Delta\nu_{1/2}$ = 66 Hz), 33.3 (s, 3H, $\Delta\nu_{1/2}$ = 94 Hz), 31.2 (s, 3H, $\Delta\nu_{1/2}$ = 96 Hz), 9.5 (s, 6H, $\Delta\nu_{1/2}$ = 24 Hz), 6.8 (s, 3H, $\Delta\nu_{1/2}$ = 72 Hz), 6.4 (s, 3H, $\Delta\nu_{1/2}$ = 53 Hz), 5.7 (s, 3H, $\Delta\nu_{1/2}$ = 71 Hz), 1.9 (s, 9H, $\Delta\nu_{1/2}$ = 114 Hz), 0.6 (s, 9H, $\Delta\nu_{1/2}$ = 103 Hz), and −3.3 ppm (s, 3H, $\Delta\nu_{1/2}$ = 24 Hz). Elemental analysis (%) calcd for $C_{39}H_{45}N_7CoCl_2$: C 63.16, H 6.11, N 13.22. Found: C 63.17, H 5.88, N 13.16.

[(TIMEN^{xyl})Co(CH$_3$CN)](BPh$_4$)$_2$ (4). (Method A) NaBPh$_4$ (2 equiv) was added to a blue solution of [(TIMEN^{xyl})CoCl]Cl (120 mg, 0.16 mmol) in acetonitrile, and the mixture was filtered through Celite. Blue crystals start to form from this filtrate within 30 min. The crystals are collected by filtration, washed with diethyl ether, and dried in a vacuum (168 mg; yield 80%).

(Method B) Excess NaBPh$_4$ was added into a yellow solution of [(TIMEN^{xyl})Co]Cl (30 mg, 0.04 mmol) in acetonitrile. The solution gradually turns blue, and blue needlelike crystals form within 1 day. The crystals were collected by filtration, washed with diethyl ether, and dried in a vacuum (20 mg; yield 38%).

^{1}H NMR (300 MHz, DMSO-d_3, 20 °C): δ 98.3 (s, 3H, $\Delta\nu_{1/2}$ = 15 Hz), 30.7 (s, 3H, $\Delta\nu_{1/2}$ = 42 Hz), 19.6 (s, 3H, $\Delta\nu_{1/2}$ = 20 Hz), 12.5 (s, 9H, $\Delta\nu_{1/2}$ = 15 Hz), 7.8 (s, 3H, $\Delta\nu_{1/2}$ = 33 Hz), 7.16 (m, 16H), 6.92 (m, 16H), 6.80 (dd, 8 H), 4.3(s, 6H, $\Delta\nu_{1/2}$ = 29 Hz), 1.3 (s, 9H, $\Delta\nu_{1/2}$ = 35 Hz), −3.2 (s, 3H, $\Delta\nu_{1/2}$ = 8 Hz), and −6.0 ppm (s, 3H, $\Delta\nu_{1/2}$ = 7 Hz). Elemental analysis (%) calcd for $C_{89}H_{88}N_8B_2Co$: C 79.17, H 6.57, N 8.30. Found: C 80.69, H 6.11, N 7.53.

[(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ (5). NaBPh$_4$ (1 equiv) was added to a suspension of [(TIMEN^{xyl})Co]Cl (100 mg, 1.4 mmol) in 3 mL of THF. All solid dissolved immediately, and the resulting solution was filtered and transferred to a Schlenk flask. The flask was evacuated and cooled to −78 °C. Neat dioxygen gas was transferred to the flask and the reaction mixture was allowed to warm to room temperature. A pale-pink solid starts to precipitate from the solution within 1 h. The solid

was collected by filtration, washed with diethyl ether, and dried in a vacuum (90 mg; yield 57%).

^{1}H NMR (300 MHz, DMSO-d_6, 20 °C): δ 7.50 (s, 3H), 7.16 (br s, 8H), 6.92 (m, 14H), 6.78 (d, ^3J(H,H) = 6 Hz, 3H), 6.75 (s, 3H), 6.71 (s, 3H), 4.25 (br s, 3H), 3.60 (br s, 3H), 3.50(br s, 3H), 2.65 (br s, 3H), 1.64 (s, 9H), and 1.25 ppm (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C): δ 164.8, 164.3, 163.8, 163.3, 140.6, 136.2, 135.3, 127.6, 127.4, 126.1, 126.0, 125.9, 125.7, 123.5, 122.2, 47.7, 18.6, and 17.8 ppm. IR(KBr): ν(OO) = 890 cm^{-1}. Elemental analysis (%) calcd for $C_{73}H_{65}N_7BO_2Co$: C 76.77, H 5.70, N 8.59. Found: C 76.34, H 5.43, N 8.28.

The ^{18}O-labeled [(TIMEN^{xyl})Co(^{18}O$_2$)]BPh$_4$ complex was synthesized employing 95% ^{18}O$_2$-labeled gas.

Reactions of [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ with Benzoyl Chloride. Benzoyl chloride (1 equiv) was added to a stirred solution of **5** (30 mg, 0.026 mmol) in acetonitrile. The reaction was allowed to stir for 1 day, and the resulting blue solution was evaporated to dryness. Diethyl ether was added to extract the organic product, which, after workup, was identified as phenyl benzoate by IR, NMR, and GC-MS. The solid residue was also collected and identified as complex **4** by NMR spectroscopy (30 mg; yield 79%). The same reaction products were isolated when excess benzoyl chloride was used. NMR reaction showed that **4** was the only tractable cobalt complex formed.

Reactions of [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ with Benzylidenemalo-nitrile. Benzylidenemalonitrile (1 equiv) was added to a solution of **5** (15 mg, 0.013 mmol) in acetonitrile under stirring. A blue solution formed in 30 min. The solution was evaporated to dryness and diethyl ether was added to extract the organic product, which contains benzyl aldehyde as evidenced by NMR and GC-MS. The solid residue was also collected and identified as complex **4** by its NMR spectrum (10 mg; yield 53%). NMR reaction showed that **4** is the only tractable cobalt complex formed.

Reactions of [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ with TCNE. Benzylidene-malonitrile (1 equiv) was added to a stirred solution of **5** (15 mg, 0.013 mmol) in acetonitrile. The resulting blue solution was evaporated to dryness and diethyl ether was added to extract any organic products. The solid residue was collected and identified as complex **4** by NMR spectroscopy (12 mg; yield 64%). An NMR reaction showed that **4** is the only tractable cobalt complex formed.

Reactions of [(TIMEN^{xyl})Co(O$_2$)]BPh$_4$ with Alkenes and Tri-phenylphosphine. The reactivity of **5** with 2-cyclohexen-1-one, 1,4-naphthaquinone, 2-methyl-1,4-naphthaquinone, styrene, cyclohexene, and triphenylphosphine was examined. In a typical reaction, an NMR tube was loaded with equal molar amounts of **5** and alkene (or phosphine) and the reaction was monitored by NMR spectroscopy. In all cases, no change in the NMR spectrum was observed after 2 days.

Crystallographic Details for [(TIMEN^{xyl})Co(CO)]Cl·2CH$_3$CN (2· 2CH$_3$CN). A crystal of dimensions 0.41 × 0.33 × 0.08 mm^3 was mounted on a glass fiber. A total of 17 360 reflections ($-13 \le h \le$ 13, $-13 \le k \le 13$, $-27 \le l \le 26$) were collected at $T = 100(2)$ K in the range of 0.97−27.51°, of which 8901 were unique ($R_{int} = 0.0190$); Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods (Shelxtl version 6.10, Bruker AXS, Inc., 2000). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The residual peak and hole of electron densities were 0.740 and −0.344 eA^{-3}. The absorption coefficient was 0.527 mm^{-1}. The least-squares refinement converged with residuals of $R(F) = 0.0367$, $wR(F^2) = 0.0903$, and a GOF = 1.033 [$I > 2\sigma(I)$]. $C_{44}H_{51}ClCoN_9O$, space group $P\bar{1}$, triclinic, $a = 10.5775(9)$, $b = 10.6288(9)$, $c = 21.2014(9)$, $\alpha = 94.2400(10)°$, $\beta = 93.0000(10)°$, $\gamma = 119.2060(10)°$, $V = 2064.1(10)$ A^3, $Z = 2$, $\rho_{calcd} = 1.313$ Mg/m^3.

Crystallographic Details for [(TIMEN^{xyl})Co(Cl)]Cl·DMSO (3· DMSO). A crystal of dimensions 0.30 × 0.13 × 0.02 mm^3 was mounted on a glass fiber. A total of 11 898 reflections ($-11 \le h \le$ 11, $-11 \le k \le 11$, $-22 \le l \le 22$) were collected at $T = 100(2)$ K in the range of 1.98−22.50° of which 5352 were unique ($R_{int} = 0.0259$);

Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct methods (Shelxtl version 6.10, Bruker AXS, Inc., 2000). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The cocrystallized DMSO solvent molecule was disordered and, therefore, modeled on two positions. The residual peak and hole of electron densities were 1.682 and -0.429 eA^{-3}. The absorption coefficient was 0.643 mm^{-1}. The least-squares refinement converged with residuals of $R(F) = 0.0618$, $wR(F^2) = 0.1654$, and a GOF = 1.071 [$I > 2\sigma(I)$]. $C_{41}H_{45}Cl_2CoN_7OS$, space group $P\bar{1}$, triclinic, $a = 10.667(2)$, $b = 10.702(2)$, $c = 20.707(4)$, $\alpha = 87.212(3)°$, $\beta = 83.314(3)°$, $\gamma = 60.477(3)°$, $V = 2062.7(7)$ A^3, $Z = 2$, $\rho_{calcd} = 1.323$ Mg/m^3.

Crystallographic Details for [(TIMEN^{xyl})Co(CH$_3$CN)](BPh$_4$)$_2$·CH$_3$CN (4·CH$_3$CN). A crystal of dimensions $0.40 \times 0.10 \times 0.05$ mm^3 was mounted on a glass fiber. A total of 42 407 reflections ($-25 \leq h \leq 25$, $-12 \leq k \leq 12$, $-29 \leq l \leq 29$) were collected at $T = 100(2)$ K in the range of $1.98-22.50°$ of which 9860 were unique ($R_{int} = 0.0697$); Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct methods (Shelxtl version 6.10, Bruker AXS, Inc., 2000). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The residual peak and hole of electron densities were 0.476 and -0.249 eA^{-3}. The absorption coefficient was 0.282 mm^{-1}. The least-squares refinement converged with residuals of $R(F) = 0.0491$, $wR(F^2) = 0.1065$, and a GOF = 1.049 [$I > 2\sigma(I)$]. $C_{91}H_{91}B_2CoN_9$, space group $P2_1/c$, monoclinic, $a = 23.7912(19)$, $b = 11.5916(9)$, $c = 27.394(2)$, $\alpha = 90°$, $\beta = 94.8400(10)°$, $\gamma = 90°$, $V = 7527.6(10)$ A^3, $Z = 4$, $\rho_{calcd} = 1.228$ Mg/m^3.

Crystallographic Details for [(TIMEN^{xyl})Co(O$_3$)]BPh$_4$·Et$_2$O (5·Et$_2$O). A crystal of dimensions $0.21 \times 0.10 \times 0.03$ mm^3 was mounted on a glass fiber. A total of 20 992 reflections ($-16 \leq h \leq 16$, $-17 \leq$ $k \leq 17$, $-19 \leq l \leq 19$) were collected at $T = 100(2)$ K in the range of $1.34-25.0°$ of which 10 206 were unique ($R_{int} = 0.065$); Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct methods (Shelxtl version 6.10, Bruker AXS, Inc., 2000). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. Two sites occupied by diethyl ether were identified in the unit cell. The sites were considerably disordered and were treated by SQUEEZE[95] as a diffuse contribution. In the resulting void space, a contribution of 115 e$^-$/unit cell was found (required, 84 e$^-$). The residual peak and hole of electron densities were 0.670 and -0.355 eA^{-3}. The absorption coefficient was 0.341 mm^{-1}. The least-squares refinement converged with residuals of $R(F) = 0.0650$, $wR(F^2) = 0.1356$, and a GOF = 0.953 [$I > 2\sigma(I)$]. $C_{63}H_{65}BCoN_7O_2$, space group $P\bar{1}$, triclinic, $a = 13.600(3)$, $b = 14.788(3)$, $c = 16.356(3)$, $\alpha = 95.254(3)°$, $\beta = 109.027(3)°$, $\gamma = 106.392(3)°$, $V = 2921.7(9)$ A^3, $Z = 2$, $\rho_{calcd} = 1.162$ Mg/m^3.

Supporting Information Available: Crystallographic details on a crystal containing a mixture of **1** and **3**, and complete listings of structural parameters for **2–5** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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