

Synthesis and Structural Features of Co(II) and Co(III) Complexes Supported by Aminotrisphenolate Ligand Scaffolds

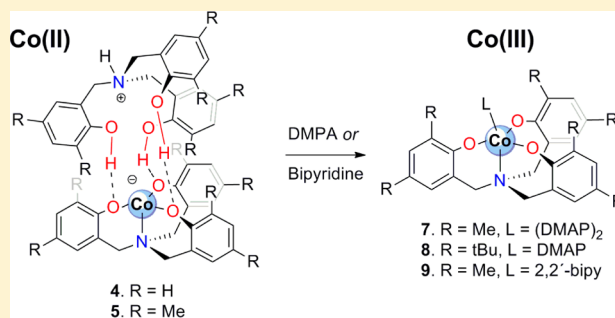
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Supporting Information

ABSTRACT: Co(II) complexes of aminotrisphenolate ((ArO)₃N³⁻) ligands can be prepared straightforwardly in high yield. X-ray analysis reveals these complexes to comprise of two different hemispheres, one containing an anionic Co((ArO)₃N)⁻ and the other a cationic (ArO)₃NH⁺ unit, which are associated through hydrogen bonding. These Co(II) complexes can be easily converted into their Co(III) analogues in air in the presence of suitable bases such as dimethylaminopyridine and 2,2'-bipyridine, and the structural features and magnetic properties of these latter compounds are also reported.



INTRODUCTION

The use of aminotrisphenolate ligands (abbreviated as (ArOH)₃N ligands) in inorganic and catalysis-related research is an active area of science with an ever-increasing impact in several communities.¹ These (ArO)₃N-chelating ligands combine a potentially multidentate coordination ability with relative ease for variation of the ligand through synthetic modulation. As such, complexes of these ligands have recently been the basis of several new catalyst systems for a variety of applications involving high-valent metals including Ti(IV),^{2a,b} V(V),^{2c} Mo(VI),^{2d} Zr/Hf(IV),^{2e} U(IV),^{2f} Fe(III),^{2g-i} and Al(III).^{2j-1} Recently, the first examples of Co(II)(ArO)₃N complexes that contain bulky *ortho*-groups attached to the ligand framework have been reported,³ as a prelude to activation of small molecules such as dioxygen. In addition to the use of these (ArO)₃N-chelating ligands, there are many examples of other tripodal (hybrid) ligands systems that have been shown to incorporate Co(II) ions,⁴ having in most cases a N₄-chelating character such as in amino-trispyridyl (TPA) ligands. However, (reactivity) studies involving the formation of Co(III) complexes of these aforementioned ligands are limited,^{4f,h,i} and to the best of our knowledge Co(III)(ArO)₃N species have thus far not been crystallographically characterized.

The chemistry of Co(III)-salen complexes has been well-developed over the years and shown to be of eminent use in catalytic operations focusing on kinetic resolution of (*rac*)-epoxides⁵ and their copolymerization with carbon dioxide (CO₂) forming useful polycarbonates,⁶ with further reports also detailing other types of catalysis with these complexes.⁷ Mechanistic studies have revealed that in these copolymerization reactions a bimetallic transition state⁸ is operative activating two substrate molecules leading to a more efficient

conversion and improved reactivity and/or selectivity behavior. We recently found that (ArO)₃N-based complexes of Fe(III)^{2g} and Al(III)^{2k} have the ability to form hexacoordinated structures with two *cis*-positioned coordination sites for incoming substrates. The effect of an external ligand or substrate on the overall conformation and fluxionality of aminotrisphenolate complexes has been reported before for Ti(IV)-based systems;⁹ Zonta et al. reported in this respect an interesting Ti(IV) peroxo complex^{9b} that, after coordination of a solvent molecule, changes its coordination geometry and enables oxygen-transfer catalysis.

Furthermore, the Fe(III) family of complexes was also shown to efficiently catalyze the formation of poly(cyclohexene)-carbonate similar to the aforementioned Co(III)-salen complexes.¹⁰ As a result we hypothesized that two available *cis*-coordination sites on a Co(III) center could be highly useful for the formation of organic carbonates from epoxides and CO₂ and therefore we started to combine our interest in (ArO)₃N ligands and the highly successful application of Co(III) chemistry to mediate these epoxide/CO₂ couplings. Herein we report the first synthesis and full structural characterization of Co(III)(ArO)₃N complexes.

RESULTS AND DISCUSSION

To access Co-centered (ArO)₃N complexes we followed a lead from Lehtonen¹¹ who prepared a Mo(VI)(ArO)₃N complex directly from the corresponding amino-trisphenol ligand and MoO₂(acac)₂ (acac = acetylacetonato). Thus, direct treatment of known ligands **1** and **2**¹² with Co(OAc)₂·4H₂O was probed

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and furnished Co(II) complexes **4** and **5** in good yields as blue solids.¹³ Compounds **4** and **5** are air-stable both in solution and solid phases (*vide infra*); both complexes crystallize conveniently from MeOH (**4–5**) and dichloromethane (DCM) (**5**), and their X-ray molecular structures were determined (Figure 1

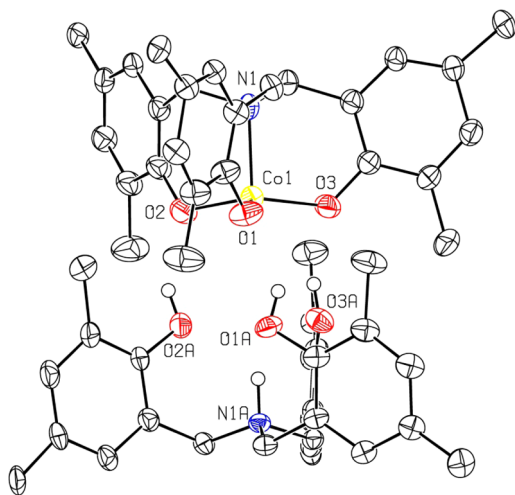


Figure 1. X-ray molecular structure for compound **5**. Selected bond lengths (Å) and angles (deg): Co(1)–O(1) = 1.897(8), Co(1)–O(2) = 1.904(8), Co(1)–O(3) = 1.899(8), Co(1)–N(1) = 2.052(10); O(1)–Co(1)–N(1) = 98.9(3), O(3)–Co(1)–N(1) = 98.5(3), O(2)–Co(1)–O(3) = 117.9(4).

and Supporting Information, Figure S39). The structure reported for compound **5** comprises of an anionic part, namely, $\text{Co}(\text{ArO})_3\text{N}^-$, and a cationic $(\text{ArO})_3\text{NH}^+$ fragment; the latter is associated with the Co(II) complex via hydrogen bonding.¹¹ As a result, the two different hemispheres give rise to a capsular system in which the metal center sits in a monopyramidal coordination geometry as was also observed by Meyer and co-workers for their comparable $\text{Co}(\text{II})(\text{ArO})_3\text{N}$ complexes.³ The observed structural parameters support that the Co center is tetracoordinated and is slightly displaced from the O_3 -plane of the ligand toward the nitrogen center N1. The overall features for the anionic part of **5** closely relate to those reported for other monopyramidal coordination geometries reported for Co(II) complexes based on other tetradentate ligand systems.^{4a,c,f,g}

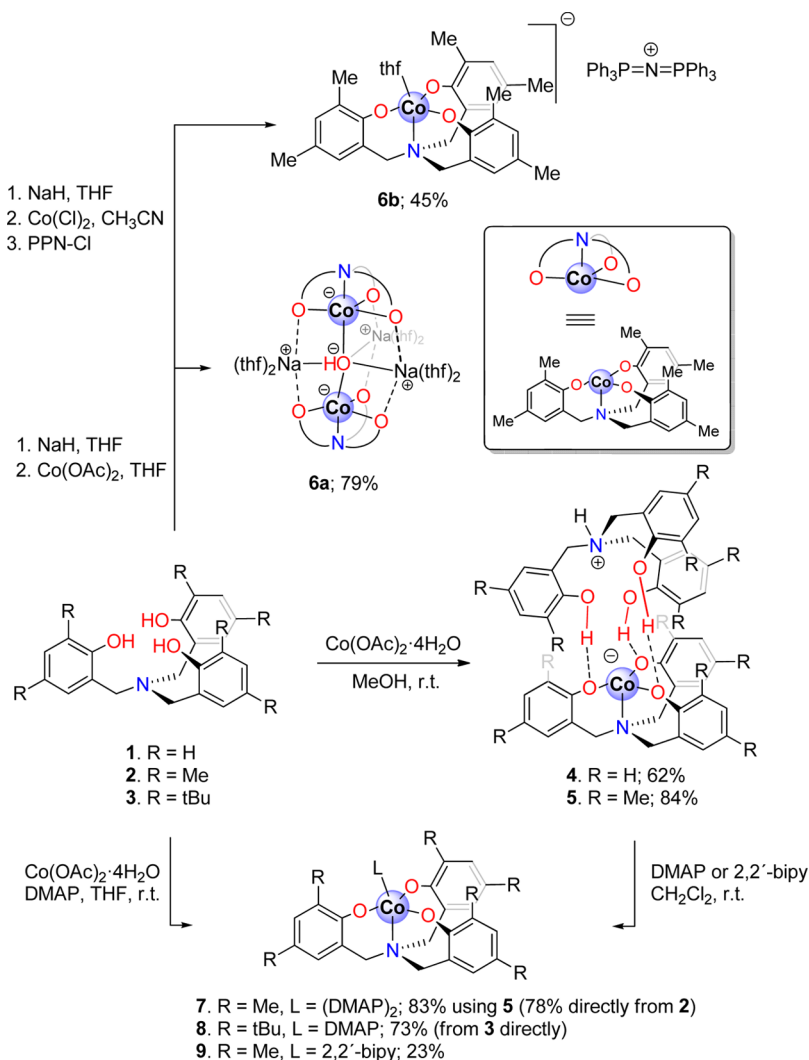
The synthetic approach towards Co(II) complexes **4** and **5** does not allow for the introduction of other cations as the aminotrisphenolate ligand $(\text{ArOH})_3\text{N}$ itself acts as a proton scavenger. The cation $(\text{ArOH})_3\text{NH}^+$ could also not be simply exchanged by addition of a NBu_4Cl or alike in separate experiments. Therefore, we probed another route toward these $\text{Co}(\text{II})(\text{ArO})_3\text{N}$ complexes by initial deprotonation of the $(\text{ArOH})_3\text{N}$ ligand using NaH followed by transmetalation of *in situ* formed $(\text{ArONa})_3\text{N}$ with $\text{Co}(\text{OAc})_2$ in tetrahydrofuran (THF). The product of this reaction, complex **6a** (79% yield, Scheme 1 and Figure 2), was isolated as a binuclear Co(II) complex that incorporates two $(\text{ArO})_3\text{N}$ ligands, three Na cations, a bridging hydroxo ligand, and six THF ligands. These results demonstrate that other cations may also be associated with the anionically charged $\text{Co}(\text{II})(\text{ArO})_3\text{N}$ complex. The presence of a hydroxo ligand (OH) can be explained by the presence of some NaOH prior to, during, and/or after the reaction as a result of the presence of adventitious water. We thus performed an alternative synthesis using anhydrous CoCl_2

as transmetalating agent, and the addition of bis-triphenylphosphineiminium chloride (PPN-Cl) provoked a cation exchange affording complex **6b** (45%). X-ray analysis of this latter complex (Figure 3) disclosed the presence of an anionic Co(II) fragment reminiscent of complexes **4** and **5** though with an solvent molecule occupying the apical position and having a noncoordinating cation associated (PPN⁺). This result shows that, at least when isolation of the Co(II) complexes is concerned, a coordinating cation is not a prerequisite.

The Co(II) complexes **4** and **5** probably gain stability by steric protection exerted by the cationic unit $(\text{ArO})_3\text{NH}^+$ that is associated with the Co(II) complex through an ionic as well as three H-bond interactions. Further evidence for this hypothesis was gained from comparative stability studies of complexes **4** and **5**, and **6b**. Interestingly, while complexes **4** and **5** seem to be stable both in the solid as well as solution phase for at least 24 h, complex **6b** shows clear signs of decomposition in the solid and solution state within 24 h after exposure to air (see Supporting Information, Figures S50 and S51). Thus, it seems that the presence of an interacting, coordinating cation may help to stabilize the Co(II) oxidation state of these kinds of complexes. Cyclic voltammetry studies that involved complex **6b** also clearly showed that oxidation is significantly more feasible for this complex as compared to complex **5** (E_p^{ox} is 0.27 V and 0.65–0.70 V, respectively; see Supporting Information).

We decided to deprotonate compound **5** to explore the opportunity to introduce other ligands. When a solution of compound **5** in CH_2Cl_2 (blue) was treated in air¹⁴ with an excess of 4-dimethylaminopyridine (DMAP) a drastic color change to dark violet was noted indicating a change in the oxidation state of the Co center and/or coordination geometry; after removal of the solvent the purple residue was recrystallized from CH_2Cl_2 /hexane to afford complex **7** in good yield (83%). X-ray analysis revealed the presence of a Co complex having two DMAP ligands incorporated in the coordination sphere in complex **7** (Figure 4). The DMAP ligands occupy an equatorial and axial position of the roughly octahedral geometry around the Co center. The structure clearly demonstrates the flexibility of the $(\text{ArO})_3\text{N}$ ligand to accommodate the formation of a hexacoordinated complex potentially useful in catalytic conversions.^{5,6}

¹H NMR studies were then first performed using **5** and **7** (Supporting Information; Figures S2 and S5–S8) to study their solution behavior. As expected, for **5** paramagnetically shifted resonances are found in the region from –48 to 36 ppm, and no significant changes were noted upon lowering the temperature. However, for complex **7** we found that the temperature had a dramatic effect on the resolution of the ¹H NMR spectrum (Supporting Information, Figure S6). At ambient temperature (25 °C) clearly paramagnetically induced ¹H NMR shifts were noted, but upon lowering the temperature to between –30 and –40 °C a fully resolved ¹H NMR spectrum was obtained, indicative of the sole presence of a diamagnetic complex. The ¹H NMR spectrum at –40 °C displays two downfield shifts for the DMAP-*ortho* hydrogens in line with the presence of two DMAP ligands in the coordination sphere of complex **7** (cf. Figure 4). We hypothesized that at higher temperatures the coordination of the DMAP ligands is fluxional leading to a paramagnetic, five-coordinate Co(III) complex with a trigonal bipyramidal (tbp) geometry. To challenge this hypothesis, we prepared complex **8** as a control compound (Scheme 1); this complex bears more sterically demanding ^tBu groups in the *ortho*-positions of the

Scheme 1. Synthesis of Co(II) and Co(III) Complexes 4–9 from Amino–Trisphenol Ligand Precursors 1–3^a

^aNote that the protonated (ArO)₃NH⁺ ligand in complexes 4 and 5 forms an ion pair with the Co(II) complex.

phenolate donors and is likely not able to allow for hexacoordination at the Co center. However, isolation of the Co(II) complex of ligand 3 was not feasible, and therefore we attempted the direct synthesis of 8 through combination of 3, Co(OAc)₂·4H₂O, and excess DMAP. An indicative color change to dark purple was noted, and fortunately, complex 8 could be conveniently isolated by recrystallization from CH₂Cl₂/CH₃CN (73% yield). Crystallographic analysis showed this complex to be pentacoordinated, comprising of one DMAP ligand occupying one axial position of a tbp coordination geometry around the Co ion (Supporting Information, Figure S40). Further to this, to block a potential dynamic behavior between penta- and hexacoordinated geometry, complex 5 was treated with a bidentate ligand (2,2'-bipyridine: 2,2'-bipy): the presence of this ligand should give rise to a structure reminiscent of complex 7 and be conformationally stable such that under ambient conditions a diamagnetic compound should prevail. Complex 9 (Scheme 1) was isolated as a brown crystalline compound (23% yield; see Supporting Information for details) and its molecular structure was determined by X-ray diffraction (Supporting Information, Figure S41). Complex 8 clearly displays ¹H NMR characteristics of a paramagnetic species at ambient and lower temperature (−40 °C; Supporting

Information, Figure S9), whereas the bipy-complex 9 gives rise to a well-resolved and defined ¹H NMR spectrum under ambient conditions (Supporting Information, Figure S10). Interestingly, the presence of a bipy-ortho-H resonance located at δ = 10.35 indicates hydrogen bonding to a phenolate–O and may thus help to further stabilize this complex.

The oxidation processes for both cobalt(II) complexes (4 and 5) investigated by cyclic voltammetry are observed at relative high potential ($E_p^{ox} = 1.05$ and around 0.7 V, respectively, vs Ag/AgCl), which supports the high stability of these complexes against oxidation (Supporting Information; Figures S42–S44). In the case of complex 4 a single quasi-reversible wave is observed, whereas complex 5 exhibits an irreversible oxidation process as a likely result of the oxidation of the (Ar^{Me}O)₃N ligand. The cyclic voltammogram (CV) for this complex showed a broad wave between 0.65–0.75 V versus Ag/AgCl due to overlapping oxidation processes that involve the Co^{II}/Co^{III} redox couple within the (Ar^{Me}O)₃N ligand and the (Ar^{Me}O)₃NH⁺ cationic unit. The CV obtained for cobalt(III) complex 7 displays, under these conditions, a reversible reduction process at $E_{1/2} = -0.09$ V versus Ag/AgCl attributed to the Co^{III}/Co^{II} couple (Supporting Information, Figure S47) and cobalt(III) compounds 8 and 9 give rise to

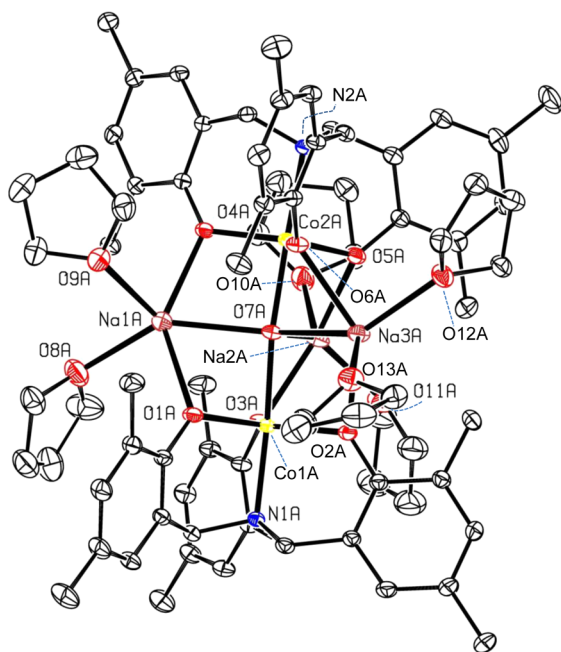


Figure 2. X-ray molecular structure for binuclear complex **6a**. Selected bond lengths (Å) and angles (deg): Co(1A)–O(1A) = 2.0008(14), Co(1A)–O(2A) = 1.9942(14), Co(1A)–O(3A) = 1.9929(15), Co(1A)–N(1A) = 2.1180(19), Co(1A)–O(7A) = 2.1056(18), Na(1A)–O(7A) = 2.4847(17), Na(2A)–O(7A) = 2.6512(19), Na(3A)–O(7A) = 2.4335(18); O(1A)–Co(1A)–O(2A) = 123.25(7), O(1A)–Co(1A)–O(3A) = 119.00(6), O(2A)–Co(1A)–O(3A) = 117.50(7), N(1A)–Co(1A)–O(7A) = 175.74(6), Co(1A)–O(7A)–Na(1A) = 47.68(4), N(1A)–Co(1A)–O(1A) = 92.03(6), Na(1A)–O(7A)–Na(2A) = 109.44(7), Na(1A)–O(7A)–Na(3A) = 145.96(8).

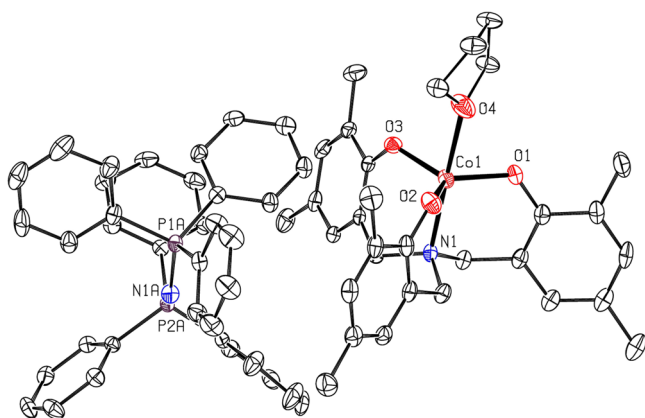


Figure 3. X-ray molecular structure for complex **6b** together with a partial numbering scheme. Selected bond lengths (Å) and angles (deg): Co(1)–O(1) = 1.953(2), Co(1)–O(2) = 1.950(2), Co(1)–O(3) = 1.949(2), Co(1)–N(1) = 2.147(3), Co(1)–O(4) = 2.204(6); O(1)–Co(1)–O(3) = 114.54(9), O(2)–Co(1)–O(3) = 120.64(9), O(1)–Co(1)–O(2) = 123.92(10), N(1)–Co(1)–O(4) = 87.37(15), N(1)–Co(1)–O(1) = 94.00(9); N(1)–Co(1)–O(3) = 92.89(9).

similar quasi-reversible CVs for the Co^{III}/Co^{II} couple at $E_{1/2} = -0.13$ and -0.05 V, respectively, versus Ag/AgCl (Supporting Information, Figures S48 and S49). From these data it seems that the DMAP ligands in complex **7** are effective in the stabilization of the Co^{III} oxidation state, whereas (Ar^{Me}O)₃NH⁺ cation in complexes **4** and **5** is able to protect the Co^{II} from low-potential oxidation.

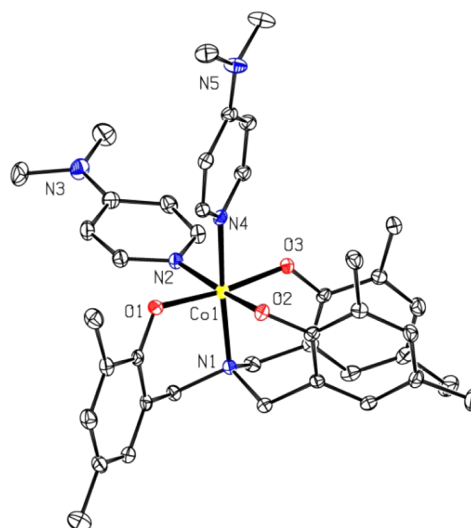


Figure 4. X-ray molecular structure for complex **7**. Selected bond lengths (Å) and angles (deg): Co(1)–O(1) = 1.9231(13), Co(1)–O(2) = 1.8985(14), Co(1)–O(3) = 1.9079(13), Co(1)–N(1) = 2.0174(16), Co(1)–N(2) = 2.0350(17), Co(1)–N(4) = 1.9783(16); O(1)–Co(1)–O(3) = 172.92(6), N(2)–Co(1)–O(2) = 172.95(6), N(1)–Co(1)–N(4) = 176.23(6).

Finally, we performed magnetic susceptibility measurements in polycrystalline samples of **4**, **5** and **7–9** (Figure 5). The $\chi_m T$

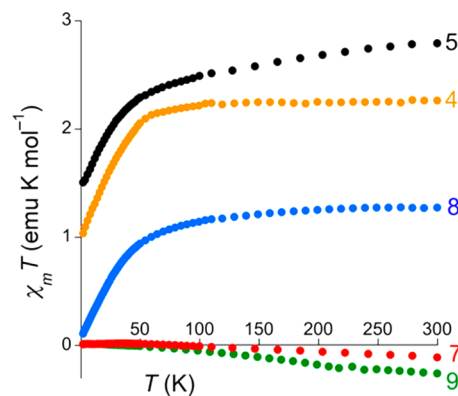


Figure 5. Temperature dependence of the $\chi_m T$ product for complexes **4**, **5**, and **7–9**.

products at room temperature (r.t.) are 2.25, 2.79, -0.11 , 1.28, and -0.26 emu K mol⁻¹, respectively. These values correspond to a $S = 3/2$ with strong spin–orbit coupling, as expected for high spin Co(II) in **4** and **5**; a diamagnetic $S = 0$, from the octahedral low-spin Co(III) in **7** and **9**; and an $S = 1$, from the two unpaired electrons expected in a Co(III) center with t_{2g} coordination in **8**.¹⁵ These are in good agreement with the ¹H NMR data. The temperature dependence of the magnetization is dominated by the zero-field splitting of the single ions.

From the r.t. values, $\chi_m T$ decreases as temperature is decreased for the paramagnetic complexes **4**, **5**, and **8**. In the case of **4**, $\chi_m T$ remains constant at 2.25 emu K mol⁻¹ to 60 K, when it drops quickly to 1.0 emu K mol⁻¹ at 2 K. In the case of **5**, $\chi_m T$ decreases slowly from 2.79 to 2.30 emu K mol⁻¹ at 50 K, and then it drops quickly to 1.5 emu K mol⁻¹ at 2 K. This behavior in **4** and **5** is typical of high-spin trigonal pyramidal Co(II) complexes, with strong spin–orbit coupling, analogous to that reported by Meyer for related Co(II) species.³ In the

case of **8**, $\chi_m T$ remains essentially constant to 80 K, and then it also drops sharply reaching $0.10 \text{ emu K mol}^{-1}$ at 2 K, due to the zero-field splitting of the triplet ground state. Complexes **7** and **9** are diamagnetic at r.t. As the temperature is decreased, $\chi_m T$ shows a linear behavior, approaching positive values. This must be due to the presence of paramagnetic impurities that represent less than 3% of the complexes.

CONCLUSION

In summary, we here present an easy route toward Co(III)-(ArO)₃N complexes and their full characterization using a variety of analytical techniques. The straightforward dependence of the coordination geometry around the Co ion on the ligand substitution in these complexes allows for penta- and/or hexacoordinated metal centers. In the hexacoordinated Co(III) complexes **7** and **9** the presence of two *cis*-positioned N-donor ligands suggests that these complexes may be of value in catalytic transformations such as the copolymerization of epoxides and CO₂. However, this may be true only when suitable ligands or substrates are involved that can facilitate the oxidation of the Co(II) complex. The catalytic CO₂/epoxide coupling reactions are currently under investigation.

EXPERIMENTAL SECTION

General Considerations. All reagents were purchased from commercial suppliers and used as received. All solvents were of reagent grade and used without any further purification. The ligands H₃L^H, H₃L^{Me}, and H₃L^{Bu} (compounds **1–3**) were prepared according to literature methods.^{12,16} Elemental Analysis was performed by the Unidad de Análisis Elemental at the Universidad de Santiago de Compostela (Spain). Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) analyses (matrix = *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (dctb)) and X-ray diffraction studies were carried out by the Research Support Group at the ICIQ. Fourier transform infrared measurements were performed on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam splitter at 4 cm^{-1} resolution. UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D2 and W light sources. NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual NMR solvent signals.

Synthesis of [(Ar^HO)₃NCo]⁺[(Ar^HOH)₃NH]⁺, Complex (4**).** To a solution of the ligand tris(2-hydroxybenzyl)amine (Ar^HOH)₃N **1** (201.0 mg, 0.6 mmol, 2 equiv) in methanol (10 mL) was added a solution of Co(OAc)₂·4H₂O (77.0 mg, 0.3 mmol, 1 equiv) in methanol (10 mL). The mixture was stirred at r.t., and after 1 h, a crystalline blue solid precipitated. The blue complex was filtered off, washed with methanol, and dried. Yield: 145.7 mg (0.19 mmol, 62%). The crystalline complex **4** thus obtained from the reaction described above was suitable for X-ray crystallographic analysis. ¹H NMR (CDCl₃, 400 MHz, r.t.): paramagnetic spectrum, $\delta = 32.46, 16.35, 10.00, 6.52, 4.73, 1.33, -8.98, -12.89, -43.30$; MALDI(+)-MS (dctb): $m/z = 336.2$ [(Ar^HOH)₃NH]⁺ (calcd 336.2), MALDI(-)-MS (dctb): $m/z = 391$ [(Ar^HO)₃NCo]⁺ (calcd. 391). Anal. Calcd for C₄₂H₄₀CoN₂O₆·MeOH: C 67.98, H 5.84, N 3.69; found: C 68.03, H 5.62, N 3.86%. IR (cm⁻¹): 1593, 1478, 1456, 1265, 1248, 879, 751, 731, 596, 568, 479; UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 338 nm (155), 572 nm (230), 606 nm (260), 624 nm (225).

Synthesis of [(Ar^{Me}O)₃NCo]⁺[(Ar^{Me}OH)₃NH]⁺, Complex (5**).** To a solution of the ligand tris(2-hydroxy-4,6-dimethylbenzyl)amine (Ar^{Me}OH)₃N **2** (419.0 mg, 1.0 mmol, 2 equiv) in methanol (15 mL) was added a solution of Co(OAc)₂·4H₂O (124.0 mg, 0.5 mmol, 1 equiv) in methanol (15 mL). The mixture was stirred at r.t., and after 1 h a blue solid precipitated. The blue complex was filtered off, washed with methanol, and dried. Yield: 375.5 mg (0.4 mmol, 84%). Crystals suitable for X-ray crystallographic analysis were obtained by diffusing

hexane into a solution of **1** in dichloromethane. The sample for microanalysis was crystallized from MeOH. ¹H NMR (CD₂Cl₂, 500 MHz, r.t.): paramagnetic spectrum, $\delta = 35.65, 27.11, 25.14, 9.30, 6.15, 3.46, 1.78, 1.53, 0.88, -7.80, -11.10, -48.45$; MALDI(+)-MS (dctb): $m/z = 420.5$ [(Ar^{Me}OH)₃NH]⁺ (calcd 420.3), MALDI(-)-MS (dctb): $m/z = 475.1$ [(Ar^{Me}O)₃NCo]⁺ (calcd 475.2). Anal. Calcd for C₅₄H₆₄CoN₂O₆·1.5MeOH: C 70.61, H 7.47, N 2.97; found: C 70.59, H 7.52, N 2.95%. IR (cm⁻¹): 2916, 2856, 1494, 1474, 1436, 1254, 1208, 1161, 860, 800, 615, 473 (m); UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 346 nm (225), 570 nm (230), 604 nm (245), 624 nm (205).

Synthesis of [(Ar^{Me}O)₃NCo]₂(OH)(Na)₃(THF)₆, Complex (6a**).** A suspension of sodium hydride (64.0 mg, 2.7 mmol, 3.5 equiv) in 15 mL of THF was added dropwise into a Schlenk flask containing a solution of tris(2-hydroxy-4,6-dimethylbenzyl)amine (Ar^{Me}OH)₃N ligand (314.0 mg, 0.75 mmol, 1 equiv) in 15 mL of THF. The mixture was stirred at r.t. for 2 h, and then it was added into a Schlenk flask containing Co(OAc)₂·4H₂O (186.0 mg, 0.75 mmol, 1 equiv). After 12 h of stirring at r.t., the solution was filtered through Celite, and complexes were obtained as crystalline solids at r.t. by concentration of the solution. Yield: 305.0 mg (0.29 mmol, 79%). ¹H NMR (CDCl₃, 400 MHz, r.t.): paramagnetic spectrum, $\delta = 36.10, 30.11, 22.65, 6.39, 3.69, 1.96, 1.77, 1.12, 0.34$. MALDI(-)-HRMS (dctb): $m/z = 1013.2902$ [M-Na]⁺ (calcd 1013.2938). Anal. Calcd for C₅₄H₆₁Co₂N₂Na₃O₇·2THF: C 63.05, H 6.57, N 2.37; found: C 62.55, H 7.03, N 2.28%. IR (cm⁻¹): 2962, 2907, 1259, 1086, 1016, 796; UV-vis (CH₂Cl₂, 0.4 mM, 25 °C, $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 398 nm (4940), 490 nm (3200), 698 (695), 1032 (475).

Synthesis of [(Ar^{Me}O)₃NCo]⁺[PPN]⁺, Complex (6b**).** A suspension of sodium hydride (53.0 mg, 2.2 mmol, 3 equiv) in 10 mL of THF was added dropwise into a Schlenk flask containing a solution of tris(2-hydroxy-4,6-dimethylbenzyl)amine (Ar^{Me}OH)₃N ligand (300.0 mg, 0.72 mmol, 1 equiv) in 10 mL of THF. The mixture was stirred at r.t. for 2 h. After this time, 0.95 equiv of anhydrous CoCl₂ (88.0 mg, 0.68 mmol) in 10 mL of acetonitrile was added. The reaction mixture was stirred at r.t. for 18 h, and then it was filtered through Celite. The solution obtained was added into a Schlenk flask containing 1 equiv of bis(triphenylphosphine)iminium chloride, PPN-Cl, (0.7 mmol, 402 mg) to exchange the cation. After 6 h, the mixture was filtered through a path of Celite. The complex was obtained as a crystalline solid suitable for X-ray crystallographic analysis by concentration of the solution and by addition of hexane (v/v = 1:1). Yield: 335.0 mg (0.14 mmol, 45%). ¹H NMR (CD₂Cl₂, 400 MHz, r.t.): paramagnetic spectrum, $\delta = 37.85, 28.57, 27.90, 7.57, 7.43, 3.66, 1.98, 1.40$; MALDI(+)-MS (dctb): $m/z = 538.3$ [PPN]⁺ (calcd. 538.2), MALDI(-)-MS (dctb): $m/z = 475.1563$ [(Ar^{Me}O)₃NCo]⁺ (calcd. 475.1559). Anal. Calcd for C₆₃H₆₀CoN₂O₃P₂·THF·1/2CH₃CN·2H₂O: C 71.47, H 6.48, N 3.06; found: C 71.65, H 6.69, N 2.84%. The presence of both solvents (THF and CH₃CN) and their 2:1 ratio is supported by ¹H NMR of the dried isolated complex; see Supporting Information. IR (cm⁻¹): 3056, 2962, 2913, 2859, 1608, 1588, 1480, 1469, 1435, 1358, 1308, 1244, 1183, 1161, 1113, 1060, 1027, 997, 904, 860, 801, 749, 721, 690, 605, 549, 532, 495,423; UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, $\epsilon = \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 348 nm (725), 580 nm (330), 605 nm (335), 622 nm (325).

Synthesis of (Ar^{Me}O)₃NCo(DMAP)₂, Complex (7**).** A solution of 4-dimethylaminopyridine (DMAP) in 10 mL of dichloromethane (102.5 mg, 0.84 mmol, 2.5 equiv) was added to a round-bottom flask containing a blue solution of complex **5** (300.0 mg, 0.34 mmol, 1 equiv) in DCM (10 mL). The mixture was stirred in the presence of air at r.t. for 8 h. Then the solvent was removed to give a purple residue. The resulting compound was recrystallized from a mixture of dichloromethane/hexane (1:1 v/v) to give purple crystals. Yield: 200.0 mg (0.28 mmol, 83%). Synthesis in an inert atmosphere (either N₂ or argon) under similar conditions yields 17% of the Co(III) complex **7**. ¹H NMR (CD₂Cl₂, 500 MHz, r.t.): paramagnetic spectrum, $\delta = 54.94, 48.74, 41.09, 25.42, 8.24, 6.51, 3.00, 1.71, 1.26, -10.61, -53.61$; ¹H NMR (CD₂Cl₂, 500 MHz, 233 K): diamagnetic spectrum, $\delta = 8.53$ (d, ³J = 6.0 Hz, 2H, CH_{pyr}), 8.13 (d, ³J = 6.0 Hz, 2H, CH_{pyr}), 6.61 (d, ³J = 6.0 Hz, 2H, CH_{pyr}), 6.54 (s, 2H, CH_{Ar}), 6.52 (s, 2H, CH_{Ar}), 6.38 (d, ³J

= 6.0 Hz, 2H, CH_{pyr}), 6.12 (s, 1H, CH_{Ar}), 5.84 (s, 1H, CH_{Ar}), 4.13 (d, ²J = 12.0 Hz, 2H, ArCH₂N), 3.08 (s, 6H, NCH₃), 3.01 (s br, 2H, ArCH₂N), 2.94 (s, 6H, NCH₃), 2.86 (d, ²J = 12.0 Hz, 2H, ArCH₂N), 2.11 (s, 6H, ArCH₃), 2.02 (s, 6H, ArCH₃), 1.68 (s, 3H, ArCH₃), 1.53 (s, 3H, ArCH₃); ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz, 233 K): δ = 160.5 (C_q), 159.5 (C_q), 154.3 (C_q), 154.1 (C_q), 150.5 (CH_{pyr}), 150.1 (CH_{pyr}), 130.6 (CH_{Ar}), 130.0 (C_q), 129.8 (C_q), 129.1 (CH_{Ar}), 128.7 (C_q), 127.4 (CH_{Ar}), 126.9 (CH_{Ar}), 123.3 (C_q), 121.1 (C_q), 120.4 (C_q), 107.0 (CH_{pyr}), 105.2 (CH_{pyr}), 66.0 (ArCH₂N), 61.2 (ArCH₂N), 39.4 (NCH₃), 39.3 (NCH₃), 20.6 (ArCH₃), 20.3 (ArCH₃), 17.8 (ArCH₃), 17.1 (ArCH₃); electrospray ionization (ESI)(+)-MS (CH₃CN): *m/z* = 720.2 [M + H]⁺ (calcd 720.3), 598.2 [M-DMAP+H]⁺ (calcd. 598.2), 476.1 [M-2DMAP+H]⁺ (calcd 476.2); Anal. Calcd for C₄₁H₅₀CoN₃O₃·2H₂O: C 65.15, H 7.20, N 9.27; found: C 64.90, H 7.02, N 9.13%. IR (cm⁻¹): 2983, 2904, 2852, 1614, 1530, 1469, 1440, 1383, 1271, 1219, 1009, 949, 806, 736, 499, 428 (m); UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, ε = L·mol⁻¹·cm⁻¹): 330 nm (7560), 532 nm (5650), 894 nm (510).

Synthesis of (Ar^{Bu}O)₃NCo(DMAP), Complex (8). To a Schlenk flask containing a pink solution of Co(OAc)₂·H₂O (223.0 mg, 0.9 mmol, 1 equiv) in MeOH (10 mL) was added a colorless solution of tris(2-hydroxy-4,6-di-*tert*-butylbenzyl)amine (Ar^{Bu}OH)₃N ligand (600.0 mg, 0.9 mmol, 1 equiv) in THF (15 mL). The reaction was then stirred at r.t. for 2 h. After this a solution of dimethylaminopyridine (DMAP) in 10 mL of THF (244.0 mg, 2 mmol, 2.5 equiv) was added to the flask. This mixture was further stirred open to the air at r.t. overnight. Finally, the solvent was removed to obtain a purple residue. The resulting cobalt complex was purified by recrystallization using a mixture of dichloromethane/acetonitrile in a proportion of 1:1 to yield purple crystals. Yield: 550.0 mg (0.65 mmol, 73%). ¹H NMR (CD₂Cl₂, 500 MHz, r.t.): paramagnetic spectrum, δ = 49.50, 26.60, 4.98, 2.76, 1.58, 1.42, 1.31, 0.96, -9.12, -45.25; MALDI(+)-MS (dctb): *m/z* = 849.9 [M]⁺ (calcd 849.5), 727.7 [M-DMAP]⁺ (calcd 727.4; cf. Supporting Information, Figure S32), 672.7 [M-DMAP-Bu+H]⁺ (calcd. 672.4; cf. Supporting Information, Figure S32); Anal. Calcd for C₅₂H₇₆CoN₃O₃·1/2H₂O: C 72.70, H 9.03, N 4.89; found: C 72.66, H 9.31, N 4.98%. IR (cm⁻¹): 2951, 2903, 2865, 1620, 1536, 1458, 1443, 1412, 1383, 1361, 1263, 1220, 1171, 1022, 874, 834, 808, 624, 548, 536, 469 (m); UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, ε = L·mol⁻¹·cm⁻¹): 334 nm (9425), 536 nm (7550), 926 nm (795).

Synthesis of (Ar^{Me}O)₃NCo(bipy), Complex (9). A solution of 2,2'-bipyridine (bipy) in 10 mL of dichloromethane (183.0 mg, 1.17 mmol, 5.3 equiv) was added to a round-bottom flask containing a blue solution of complex 5 (200.0 mg, 0.22 mmol, 1 equiv) in dichloromethane (15 mL). The mixture was stirred at r.t. open to the air. After 3 d, the solvent was removed to obtain a brown residue, which was dissolved in acetone to obtain a brown solution and a blue precipitate (complex 5). The solution was filtered to separate the starting material from the desired product. Then, the solvent was removed, and the resulting compound was purified by trituration with diethyl ether and recrystallized from acetone to give brown crystals at r.t. Yield: 33.0 mg (0.05 mmol, 23%). ¹H NMR (CD₂Cl₂, 500 MHz, r.t.): diamagnetic spectrum, δ = 10.34 (d, ³J = 5.0 Hz, 1H, CH_{pyr}), 8.20 (t, ³J = 6.0 Hz, 1H, CH_{pyr}), 8.07 (d, ³J = 7.0 Hz, 1H, CH_{pyr}), 7.86 (t, ³J = 6.0 Hz, 1H, CH_{pyr}), 7.82 (d, ³J = 7.0 Hz, 1H, CH_{pyr}), 7.61 (t, ³J = 6.0 Hz, 1H, CH_{pyr}), 6.80 (s, 1H, CH_{Ar}), 6.76 (d, ³J = 5.0 Hz, 1H, CH_{pyr}), 6.72-6.67 (m, 3H, 2CH_{Ar} and 1 CH_{pyr}), 6.66 (s, 1H, CH_{Ar}), 6.41 (s, 2H, CH_{Ar}), 3.82 (d, ²J = 10.0 Hz, 2H, ArCH₂N), 3.49 (s br, 2H, ArCH₂N), 3.24 (d, ²J = 13.0 Hz, 2H, ArCH₂N), 2.44 (s, 3H, ArCH₃), 2.13 (s, 3H, ArCH₃), 2.08 (s, 6H, ArCH₃), 1.40 (s, 6H, ArCH₃); ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz, r.t.): δ = 160.8 (C_q), 158.3 (C_q), 157.5 (C_q), 156.6 (C_q), 152.1 (CH_{pyr}), 151.5 (CH_{pyr}), 139.0 (CH_{pyr}), 138.2 (CH_{pyr}), 131.8 (C_q), 131.5 (CH_{Ar}), 130.1 (C_q), 130.0 (CH_{Ar}), 127.5 (C_q), 126.8 (CH_{Ar}), 123.7 (C_q), 123.5 (C_q), 123.1 (CH_{pyr}), 122.2 (CH_{pyr}), 120.5 (CH_{pyr}), 120.4 (CH_{pyr}), 64.9 (ArCH₂N), 61.8 (ArCH₂N), 20.4 (ArCH₃), 20.2 (ArCH₃), 19.1 (ArCH₃), 16.2 (ArCH₃); MALDI(+)-MS (dctb): *m/z* = 631.4 [M]⁺ (calcd 631.2); Anal. Calcd for C₃₇H₃₈CoN₃O₃·2H₂O: C 66.56, H 6.34, N 6.29; found: C 66.04, H 5.91, N 6.43%. IR (cm⁻¹): 2973, 2906, 2856, 1605, 1470, 1443, 1310, 1267, 1157, 1033, 854, 804, 766, 730, 607, 556, 500,

408 (m); UV-vis (CH₂Cl₂, 0.2 mM, 25 °C, ε = L·mol⁻¹·cm⁻¹): 356 nm (4307), 468 nm (2140).

X-ray Diffraction Studies. The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Data Collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX II 4K CCD area detector, a FR591 rotating anode with Mo Kα radiation, Montel mirrors and a Kryoflex low temperature device (*T* = -173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used.¹⁷ Structure Refinement: SHELXL-97-UNIX VERSION.

Crystallographic Data for Complex 5. C₆₂H₇₆CoN₃O₇, *M_r* = 1020.17, monoclinic, *C*₂, *a* = 14.3608(6) Å, *b* = 24.8788(13) Å, *c* = 16.2469(7) Å, α = γ = 90°, β = 90.053(2)°, *V* = 5804.7(5) Å³, *Z* = 4, ρ = 1.167 mg·M⁻³, μ = 0.347 mm⁻¹, λ = 0.710 73 Å, *T* = 100(2) K, *F*(000) = 2180, crystal size = 0.15 × 0.13 × 0.10 mm, θ(min) = 1.637°, θ(max) = 27.50°, 21 502 reflections collected, 12 701 reflections unique (*R*_{int} = 0.0399), goodness of fit (GOF) = 1.027, *R*₁ = 0.0867 and *wR*₂ = 0.2267 [*I* > 2σ(*I*)], *R*₁ = 0.1290 and *wR*₂ = 0.2629 (all indices), Flack parameter: *x* = 0.51(4), min/max residual density = -0.369/1.214 [e·Å⁻³]. Completeness to θ(27.50°) = 99.8%. The structure is disordered over two positions (70:30 occupancy ratio) and is a MeOH/toluene solvate.

Crystallographic Data for Complex 6a. C₇₈H₁₀₉Co₂N₂Na₃O₁₃, *M_r* = 1469.50, monoclinic, *Pn*, *a* = 13.7435(14) Å, *b* = 26.138(3) Å, *c* = 21.020(2) Å, α = γ = 90°, β = 90.337(2)°, *V* = 7550.9(13) Å³, *Z* = 2, ρ = 1.293 mg·M⁻³, μ = 0.519 mm⁻¹, λ = 0.710 73 Å, *T* = 100(2) K, *F*(000) = 3128, crystal size = 0.13 × 0.10 × 0.10 mm, θ(min) = 0.779°, θ(max) = 35.34°, 320 726 reflections collected, 48 572 reflections unique (*R*_{int} = 0.0385), GOF = 1.017, *R*₁ = 0.0370 and *wR*₂ = 0.0916 [*I* > 2σ(*I*)], *R*₁ = 0.0460 and *wR*₂ = 0.0972 (all indices), Flack parameter: *x* = 0.393(6), min/max residual density = -0.455/0.720 [e·Å⁻³]. Completeness to θ(35.34°) = 95.3%. The structure is a THF solvate, and it contains two distinct complexes in the unit cell.

Crystallographic Data for Complex 6b. C₇₅H₇₉CoN₃O₃P₂, *M_r* = 1199.26, monoclinic, *P2*(1), *a* = 14.1572(11) Å, *b* = 13.5823(12) Å, *c* = 17.1867(17) Å, α = γ = 90°, β = 107.672(3)°, *V* = 3148.8(5) Å³, *Z* = 2, ρ = 1.265 mg·M⁻³, μ = 0.377 mm⁻¹, λ = 0.710 73 Å, *T* = 100(2) K, *F*(000) = 1270, crystal size = 0.20 × 0.10 × 0.03 mm, θ(min) = 1.51°, θ(max) = 30.55°, 24 268 reflections collected, 14 719 reflections unique (*R*_{int} = 0.0265), GOF = 1.026, *R*₁ = 0.0425 and *wR*₂ = 0.0943 [*I* > 2σ(*I*)], *R*₁ = 0.0549 and *wR*₂ = 0.1005 (all indices), Flack parameter: *x* = 0.015(6), min/max residual density = -0.558/0.529 [e·Å⁻³]. Completeness to θ(30.55°) = 96.7%. The structure has a disorder in the coordinated THF molecule and cocrystallized CH₃CN, and the absolute configuration was determined.

Crystallographic Data for Complex 7. C₄₂H₅₂Cl₂CoN₅O₃, *M_r* = 804.71, triclinic, *P* $\bar{1}$, *a* = 11.4464(6) Å, *b* = 12.3420(6) Å, *c* = 15.9066(7) Å, α = 108.305(2)°, β = 99.116(2)°, γ = 104.538(2)°, *V* = 1995.11(17) Å³, *Z* = 2, ρ = 1.340 mg·M⁻³, μ = 0.609 mm⁻¹, λ = 0.710 73 Å, *T* = 100(2) K, *F*(000) = 848, crystal size = 0.15 × 0.08 × 0.04 mm, θ(min) = 1.902°, θ(max) = 28.30°, 9576 reflections collected, 9576 reflections unique, GOF = 1.039, *R*₁ = 0.0431 and *wR*₂ = 0.0999 [*I* > 2σ(*I*)], *R*₁ = 0.0586 and *wR*₂ = 0.1072 (all indices), Flack parameter: *x* = 0.393(6), min/max residual density = -0.471/0.394 [e·Å⁻³]. Completeness to θ(28.30°) = 96.4%. For this structure the program TWINABS was used¹⁸ since the two types of monocrystals had formed. The structure contains a disordered, modeled DCM molecule.

Cyclic Voltammetry. CV measurements were carried out with a Princeton Applied Research PARSTAT 2273 electrochemical analyzer. A three-component system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and Ag/AgCl (saturated NaCl) reference electrode was used. All experiments were done under argon atmosphere at r.t. and in dichloromethane solutions with 0.2 M

tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as the supporting electrolyte.

Magnetic Data. Magnetic susceptibility measurements with polycrystalline samples of complexes 4–9 were carried out in a Quantum Design MPMS-XL-7 SQUID magnetometer using a field of 1000 Oe in the 2–300 K temperature range. Pascal's constants were used to estimate the diamagnetic corrections for the compounds.

■ ASSOCIATED CONTENT

■ Supporting Information

X-ray crystallographic data in CIF format, further experimental details, and spectroscopic data of key compounds. This material is free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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