CHAPTER 6

Aluminum-Bridged Bisglyoximato Cobalt Complexes: Synthesis and Electrochemical Proton Reduction Properties

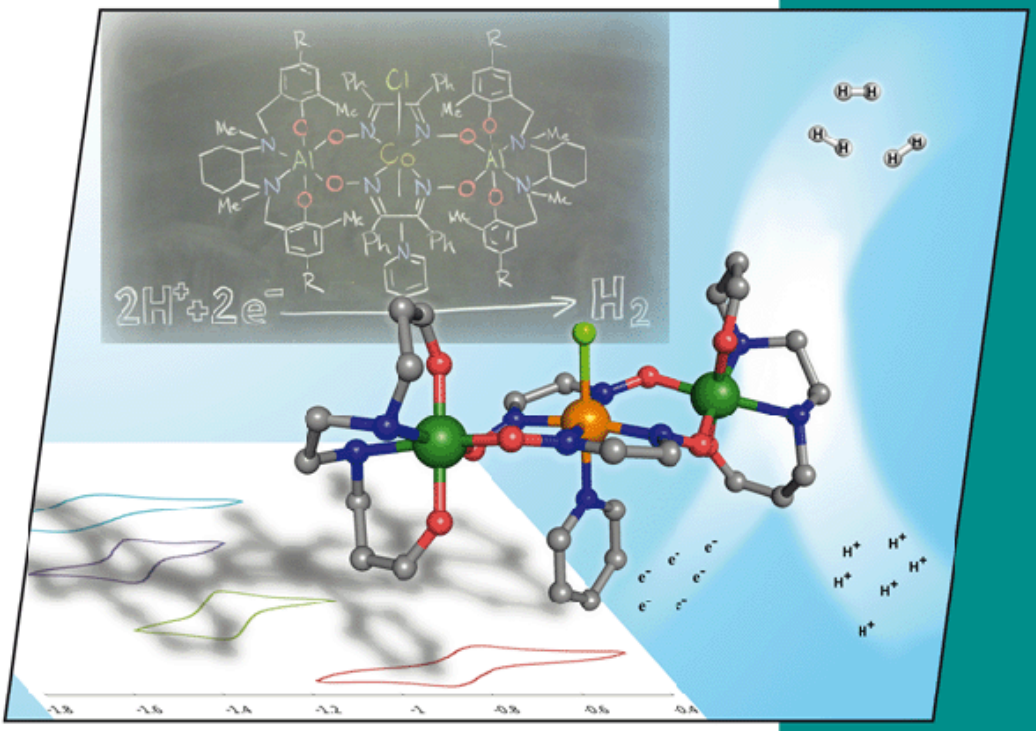
The text for this chapter was taken in part from:

Kelley, P.; Day, M. W.; Agapie, T. *Eur. J. Inorg. Chem.* 2013, *22-23*, 3840-3845.

EurJIC
European Journal of Inorganic Chemistry

22-23/2013
1st + 2nd August Issue

Cluster Issue:
Small-Molecule Activation by Reactive Metal Complexes



Front Cover Picture
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H_2 Evolution Catalyzed by Al-Bridged Cobalt Complexes

Microreviews by
Benedict M. Gardner and Stephen T. Liddle; John Arnold et al.; Kallol Ray et al.

A Journal of
ChemPubSoc Europe

WILEY-VCH
www.eurjic.org

EJICFE (22-23) 3727–4104 (2013) · ISSN 1099-0682 · No. 22-23/2013

Abstract

The syntheses of several cobalt diglyoximato complexes connected by one or two aluminum bridges are described. The aluminum centers are supported by tunable tetradentate diamine bisphenoxide ligands. Electrochemical investigations revealed that the number of aluminum bridges and the nature of the substituents on the phenoxide ligands significantly affect the cobalt reduction potentials. The present aluminium-cobalt compounds are electrocatalysts for proton reduction to dihydrogen at potentials negative of boron-and proton-bridged analogs. The reported synthetic strategies allow for modulation of reduction potentials and secondary coordination sphere interactions by tuning the ancillary ligands bound to aluminum.

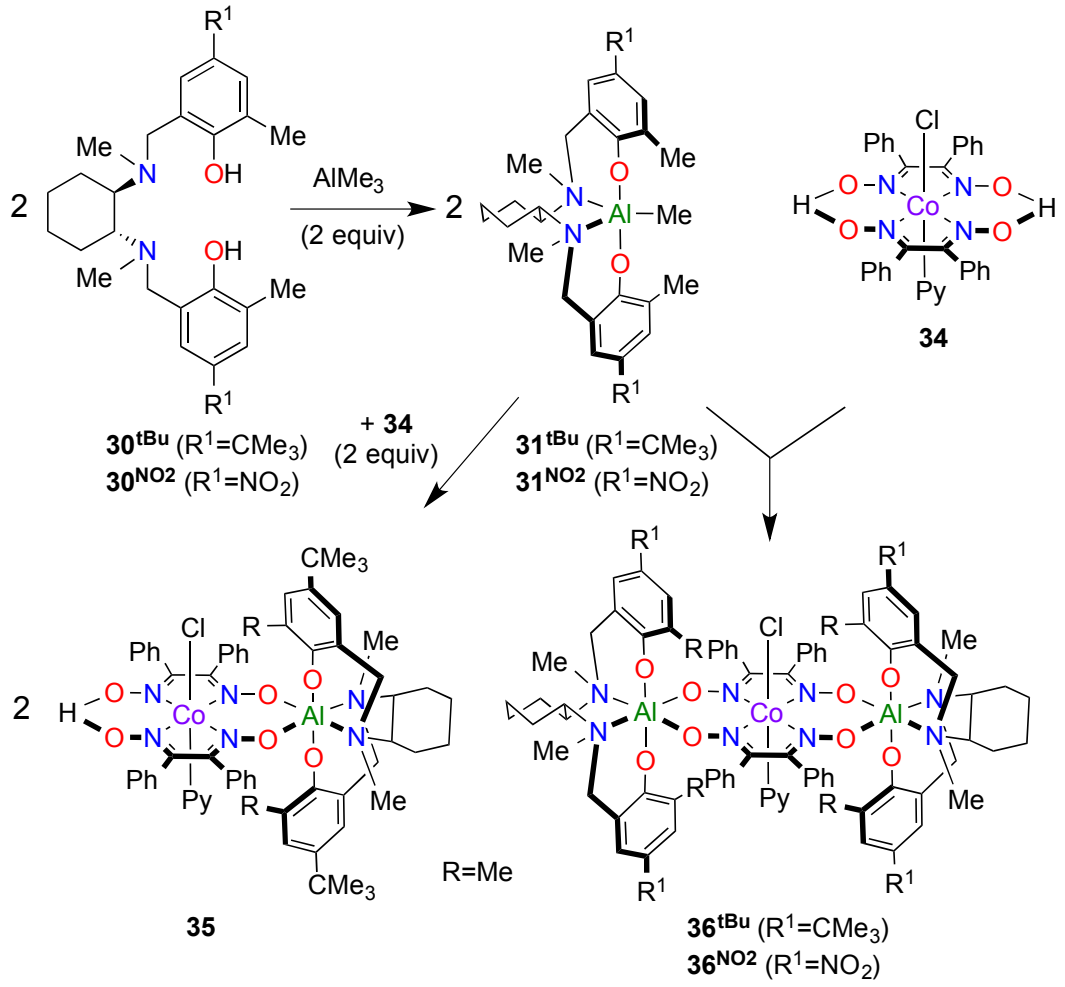
INTRODUCTION:

The reduction of protons to dihydrogen is of interest in the context of solar energy conversion and storage in chemical bonds.[1] In biological systems, this reaction is catalyzed at near thermodynamic potentials by [FeNi] and [FeFe] hydrogenases.[2] Although useful models for mechanistic studies, synthetic complexes based on hydrogenase active sites display large overpotentials and low turnover numbers.[3] Systems based on nickel tetraphosphine catalysts show high activity.[4] Several promising cobalt-based catalysts have been reported, supported by multidentate nitrogen ligands.[1c, 1d, 5] Bisglyoximato cobalt complexes, $Co(dpgX)_2(L)_2$ (dpg = diphenylglyoximato, X = H, BF_2), were reported to catalyze the reduction of protons both chemically and electrochemically.[5a-h, 6] Substitution of the protons bridging the two glyoximato groups (see complex **3**, Scheme 1) with BF_2 groups was found to affect the reduction potential of the cobalt complexes resulting in electrocatalysts active at low overpotentials.[5d-e 6a] The BF_2 moiety also imparts a greater stability towards acid in contrast to the proton-bridged species.[5d, 6j] Optimization of these catalysts has been focused either on varying the axial ligand of cobalt or the glyoxime backbone.[5d, 6a-b, 7] Herein, we report on the synthesis of bisglyoximato cobalt complexes supported by one or two aluminum-based linkers and their electrochemical properties.

RESULTS & DISCUSSION:

In analogy to the tetracoordinate boron bridges, saturated, six-coordinate aluminum linkers were targeted. Aluminum precursors having varied electronic properties were prepared, with ancillary ligands (30^{tBu} and 30^{NO2}) based on enantiopure tetradentate diamine bisphenoxide salan frameworks, starting from (*R,R*)-*trans*-1,2-diaminocyclohexane.[8] Reaction of diphenols 30^{NO2} and 30^{tBu} with $AlMe_3$ generated monoalkylaluminum diphenoxide species (31^{NO2} and 31^{tBu}, Scheme 1) as indicated by the peaks upfield of 0 ppm in the ^1H NMR spectrum assigned to the Al-CH_3 group. Monoalkylaluminum species supported by closely related ancillary ligands are formed as mixtures of inseparable isomers some of which interconvert at room temperature.[8c] Similarly, two Al-CH_3 singlets were observed for 31^{NO2}, but since the subsequent step could involve isomerizations, the mixture was used without separation.

Scheme 6.1. Synthesis of mono and dialuminum-bridged bisglyoximato cobalt complexes.



Reaction of two equivalents of $\mathbf{31}^{tBu}$ or $\mathbf{31}^{NO2}$, with cobalt diglyoximato complex **34** led to the generation of new species according to ^{1}H NMR spectroscopy. The absence of the upfield shifted singlets diagnostic of the Al-C*H*$_3$ moiety supports alkane elimination. Integrals for the *ortho* pyridine protons and the NC*H*$_3$ protons are consistent with the incorporation of two salan-supported aluminum moieties for each cobalt. The presence of four diastereotopic proton signals for the NC*H*$_2$ moieties indicates a *C*$_2$-symmetric structure, with the *C*$_2$ axis containing the cobalt center and its axial ligands. The distinct axial ligands (chloride vs pyridine) differentiate the top and bottom of the molecule, as depicted in Scheme 1. Employing the analog of **34**

displaying the dimethyl glyoxime backbone resulted in similar species (^{1}H NMR), however isolation of analytically pure samples was unsuccesfull to date due to their solubility properties.

Single crystal X-ray diffraction (XRD) studies confirmed the above structural assignment (Figure 1). The aluminum-bound glyoxime oxygen atoms are found at average O-O distances of 2.84 Å for **36^{tBu}**, 2.83 Å for **36^{NO2}**, which are significantly larger than those in H- (**3**, 2.47 Å)[9] or BF_2-linked (2.50 Å) analogs.[5e, 9b] The average Co-N distances were found to be 1.91 Å for both **36^{tBu}** and **36^{NO2}**, which are similar to those found in the H- (1.91 Å) and BF_2-linked species (1.89 Å). These structural characteristics suggest that although the macrocycles containing aluminum are larger, the effect on the Co-N distances is small. In contrast to proton- or boron-linked diglyoximato complexes that are typically planar, the cobalt-bound $N_4O_2Al_2$ macrocycle displays significant ruffling and doming distortions. The ruffling may be due to the C_2-steric strain imposed by the salan ligands found on opposite sides of the macrocycle or, as observed for porphyrins,[10] to the larger macrocycle which requires distortion to allow for binding to a central metal. The doming is likely caused by repulsive steric interaction between the pyridine and the proximal phenoxide ortho-methyl groups. Indeed, the methyl C-C distances are 7.60 and 6.86 Å on the chloride side vs 10.15 and 10.08 Å on the pyridine side, for **36^{tBu}** and **36^{NO2}**, respectively.

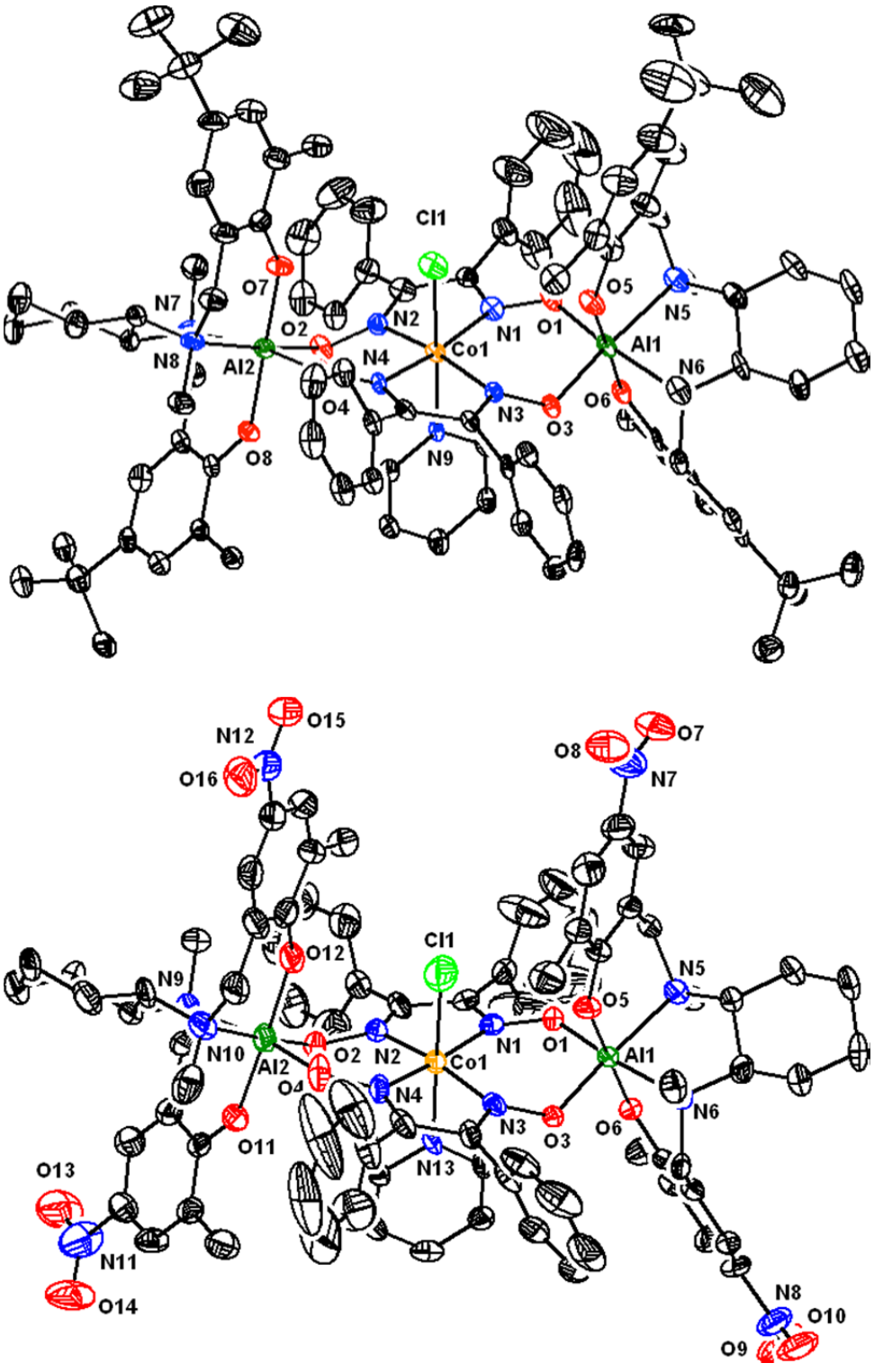


Figure 6.1. Solid state structures of 36^{tBu} and 36^{NO_2}. Hydrogen atoms and cocrystallization solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

Reaction of **34** with one equivalent of **31**^{tBu} led to the generation of a new species with NMR spectroscopic features consistent with a bimetallic cobalt-aluminum complex of *C* symmetry (**35**, Scheme 1). A downfield singlet, at 20 ppm, is indicative of the proton bridging two glyoximato units. An XRD study confirms this structural assignment and highlights the effect of bridging proton and aluminum in the same cobalt diglyoximato unit. The O-O distance is 2.38 Å on the protonated side and 2.85 Å on the aluminum side. The average Co-N distances are similar on the H- and Al-sides of the macrocycle. These are in agreement with the structural parameters observed in compounds **34** and **36**.

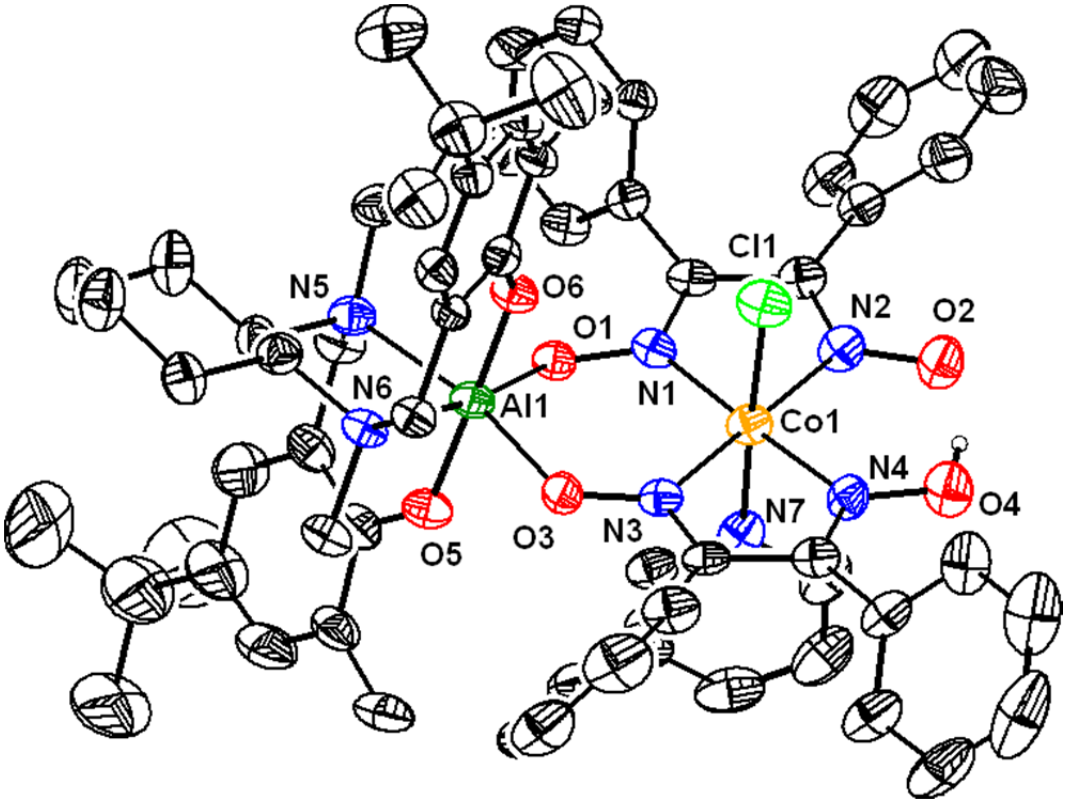
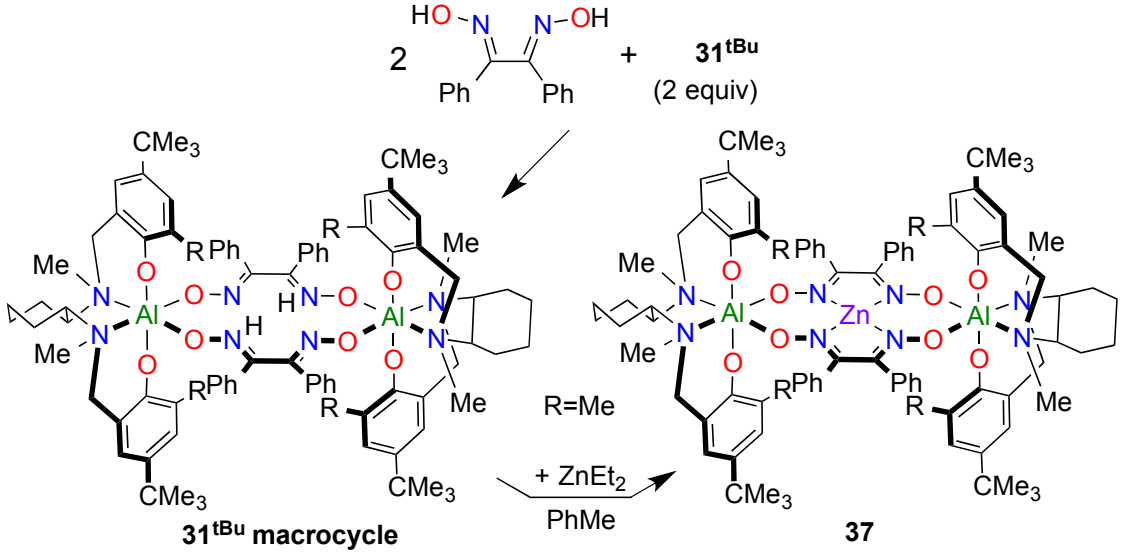


Figure 6.2. Solid state structure of **35**. Hydrogen atoms and cocrystallization solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

A dialuminum zinc analog of 36^{tBu} was targeted via a complementary synthetic protocol for comparison (Scheme 2).[11] Reaction of 31^{tBu} with diphenylglyoxime led to a species (31^{tBu} macrocycle) that displays a singlet at 14 ppm (^{1}H NMR spectrum) assigned to protonated oxime nitrogens. Treatment with diethylzinc generates a new species without any signals downfield of 8 ppm, again consistent with alkane elimination. Only two doublets are observed for the NC*H*$_2$ protons consistent with the *pseudo-D*$_2$ structure assigned to the 31^{tBu} macrocycle.

Scheme 6.2. Synthesis of dialuminum-bridged bisglyoximato zinc complex via dialuminum templation of bisglyoximato macrocycle.



The electrochemistry of the present complexes was investigated by cyclic voltametry (CV). In dimethylformamide (DMF), the Co^{II}/Co^{I} couple was observed for **35** at -1.34 V vs Fc^{+}/Fc, 36^{tBu} at -1.59 V, and 36^{NO2} at -1.35 V (Figure 6.3 and 6.4). These are the potentials at which increase in current was observed upon addition of acid (vide infra). These couples are more negative than for boron- and proton-bridged analogs.[6a] Several redox events were also observed between 0.2 and 1 V and were assigned to ligand-based processes (Figure 6.3). These waves are in the range of previously

reported electrochemical oxidations of phenoxides coordinated to redox inactive metals.[112] As expected, compound **37**, containing Zn^{II} instead of Co^{III}, shows redox events at similar potentials and no events between -2 and 0 V, consistent with lack of redox chemistry at the central atom.

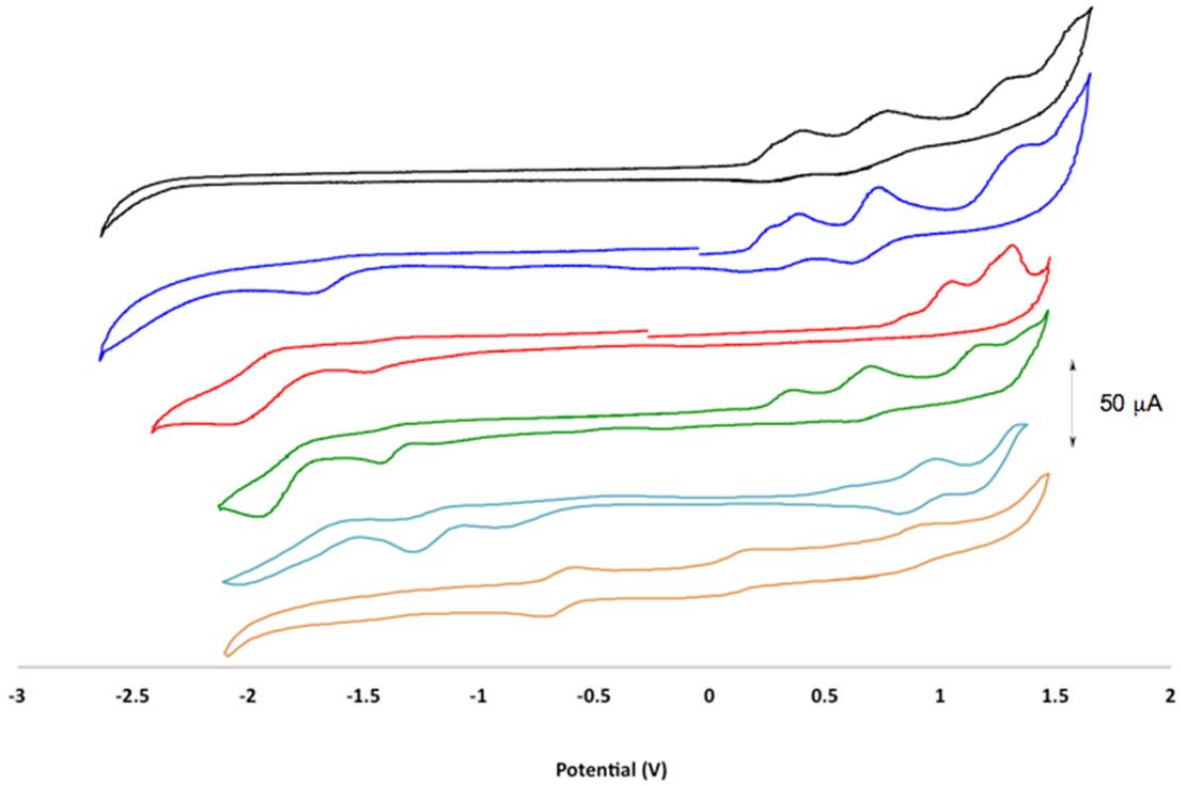


Figure 6.3. Cyclic voltammograms in 1:1 MeCN:DCM of **35** (black), $\mathbf{36}^{\mathbf{tBu}}$ (blue), $\mathbf{36}^{\mathbf{NO2}}$ (red), **37** (green), **34** (turquoise), and $\mathbf{34}^{\mathbf{BF2}}$ (orange) referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

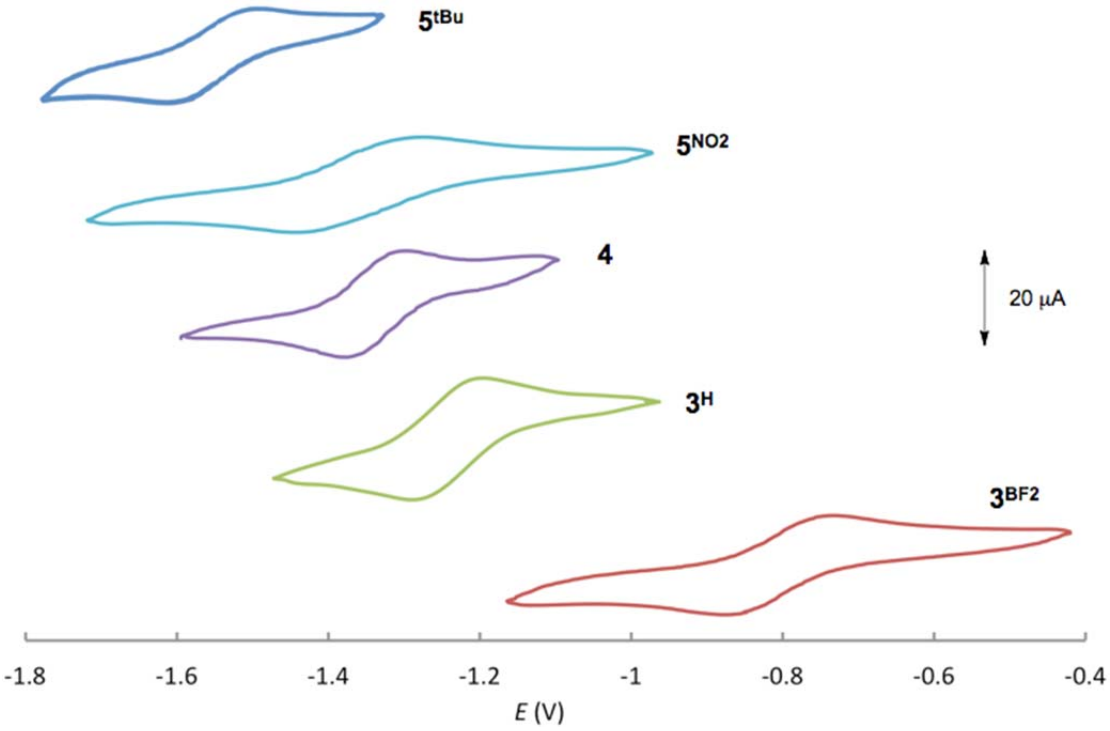


Figure 6.4. Cyclic voltammograms of the $Co^{II/I}$ couples of **36**^{tBu} (blue), **36**^{NO2} (turquoise), **35** (purple), **34**^{H} (green), and **34**^{BF2} (red) (1 mM) recorded in a 1:1 MeCN:DCM solution of $[nBu_4N][ClO_4]$ (0.1 M) at a glassy carbon working electrode using a $Ag/AgNO_3$ (0.01 M) reference electrode using a scan rate of 100 mV/s. Potentials referenced to the Fc^+/Fc couple.

Addition of trichloroacetic acid (pKa 3.5 in DMF)[13] under electrochemical conditions resulted in catalytic waves for complexes **35**, **36**^{tBu}, and **36**^{NO2} at the potentials assigned as the Co^{II}/Co^{I} couples (Figures 6.4-6.7).[5a-b, 6a] Subsequent additions of trichloroacetic acid caused cathodic shift and increase in the catalytic wave. Overpotentials were determined by comparison of the measured potential value for cobalt catalyzed proton reduction to the experimentally determined thermodynamic potential for proton reduction of trichloroacetate in DMF. Overpotentials are 680, 650, and 860 mV for the aluminum linked glyoxime complexes **35**, **36**^{tBu}, and **36**^{NO2},, respectively, and 520 and 110 mV for **34**^{H} and **34**^{BF2}, respectively with trichloroacetic acid. Bulk electrolysis experiments were performed with complexes **35** and **36**^{tBu} in a

MeCN/DCM solvent mixture, in the presence of *para*-cyanoanilinium triflate at a potential of -1.62 and -1.83 V, respectively, for two hours. Formation of H_2 was confirmed and quatified by GC analysis of the headspace. Faradaic yields of 90% and 70% were calculated for **35** and **36**^{tBu}, respectively.

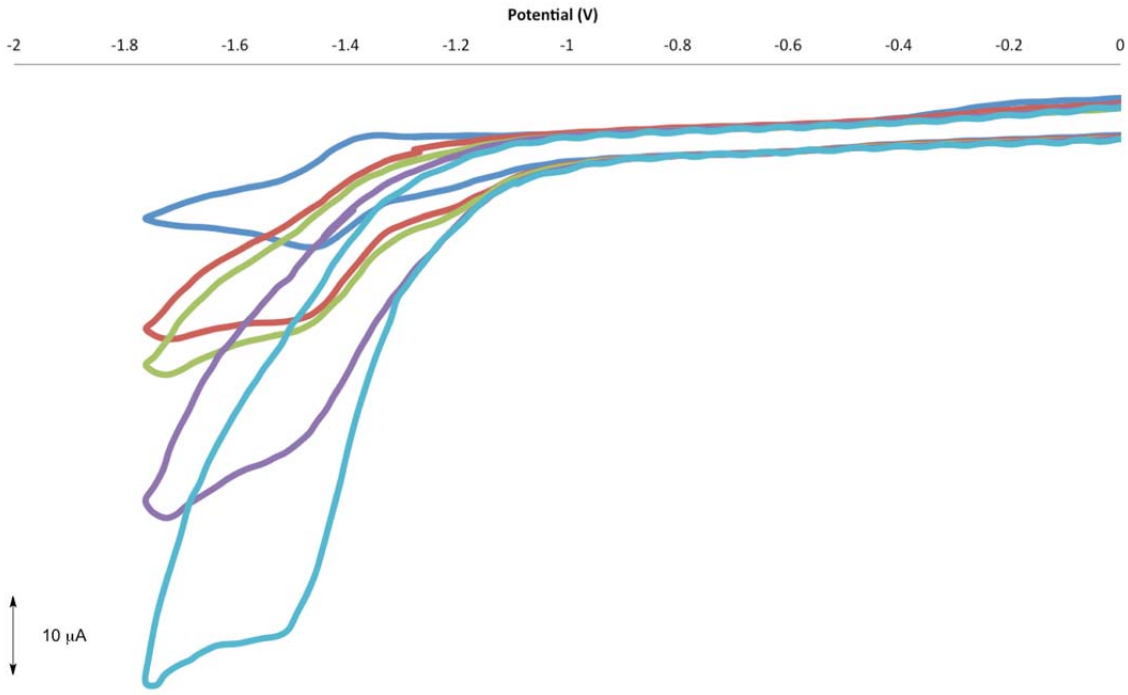


Figure 6.5. Addition of trichloroacetic acid to **35** at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (green), 11 mM acid (purple), 15 mM acid (turquoise). All waves referenced to Fc^+/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

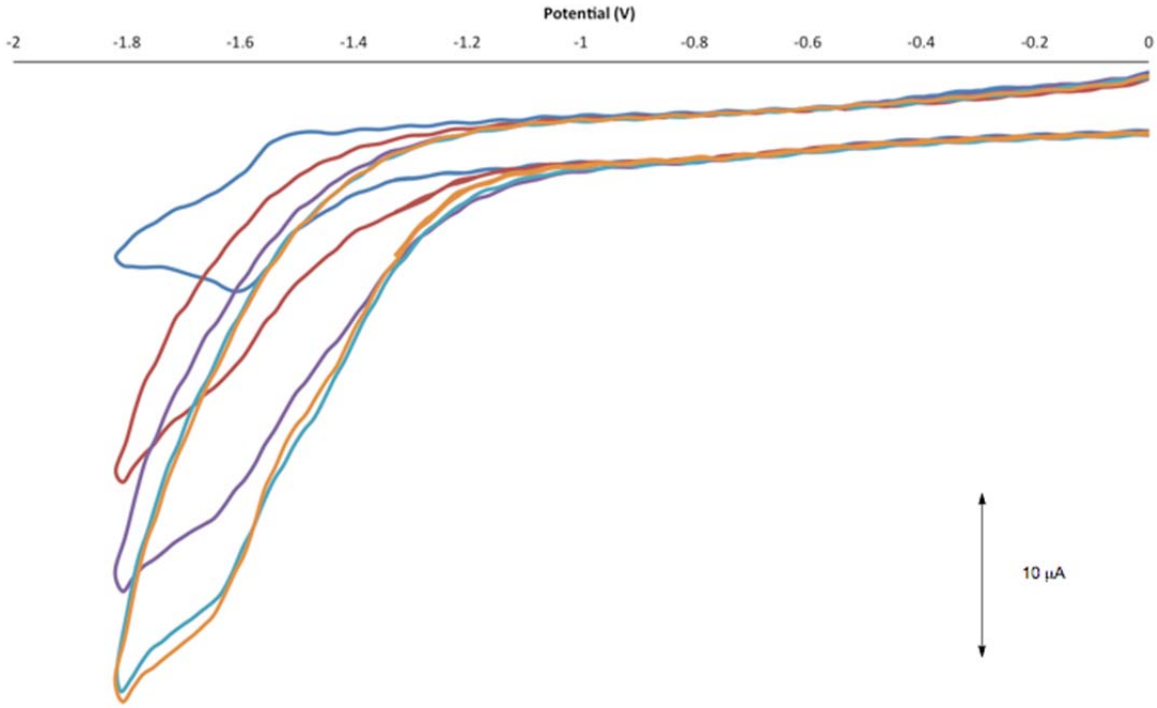


Figure 6.6. Addition of trichloroacetic acid to 36^{tBu} at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

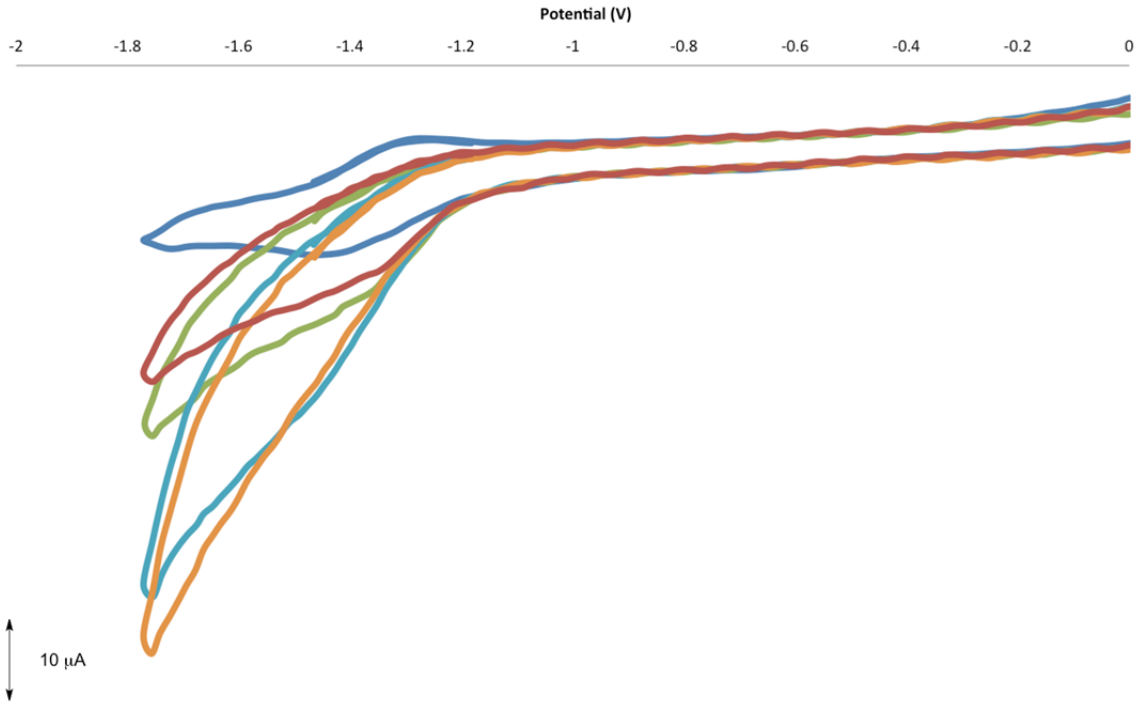


Figure 6.7. Addition of trichloroacetic acid to $\mathbf{36^{NO2}}$ at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (green), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

Table 6.1. Potentials (V) of Synthesized Complexes in DMF (0.1 M NBu_4ClO_4). Reported potentials are referenced to Fc^{+}/Fc

	$E\,Co^{II}/\,Co^{I}$	$E\,H^{+}_{red}$
$\mathbf{34^{BF2}}$	-0.80	-0.87
34	-1.24	-1.29
$\mathbf{36^{tBu}}$	-1.55	-1.64
35	-1.34	-1.50
$\mathbf{36^{NO2}}$	-1.35	-1.49

Table 6.2. Summary of Bulk Electrolysis Studies[a]

Catalyst	Potential (V vs Fc)	Duration (hr)	Charge Passed (Coulomb)[b]	Faradiac Yield for H_2 (%)	TON
4	-1.62 V	2	38	90%	16
5^{tBu}	-1.83 V	2	30	70%	12

[a] All bulk electrolysis experiments carried out with 0.1 mM catalyst and 9 mM acid in a MeCN:DCM 1:1 solution of [nBu_4N][ClO_4] (0.1 M) using glassy carbon plate working and counter electrodes with a $Ag/AgNO_3$ (0.01 M) reference electrode. [b] All values corrected for background proton reduction on the glassy carbon plate at the listed potentials. [c] TON calculated from the amount of hydrogen produced during the duration of the bulk electrolysis experiment vs catalyst in solution.

Comparison of **35** and **34** (Co^{II}/Co^{I} at -1.25 V) indicates that substitution of a proton linker with aluminum leads to a 0.14 V negative shift of the Co^{II}/Co^{I} reduction potential and onset of catalysis. Substitution of the second proton with aluminum in **36**^{tBu} led to further cathodic shift by 0.32 V. In contrast, complex **36**^{NO2} shows an anodic shift by 0.27 V compared to **36**^{tBu}. The negative shift of the Co^{II}/Co^{I} reduction potential upon incorporation of aluminum centers vs protons may be a consequence of the electron rich, multidentate diamine bisphenoxide framework coordinated to aluminum. In agreement, the analog with electron withdrawing nitro substituents shows a significant positive potential shift.

CONCLUSIONS:

In summary, the synthesis and characterization of several aluminum-bridged bisglyoximato cobalt and zinc complexes are reported. The ligands supporting the aluminum centers were found to affect the reduction potentials of cobalt and consequently the potential for proton reduction catalysis. Electrocatalytic proton reduction occurs at potentials more negative that the boron- and proton-bridged analogs. Nevertheless, the synthetic protocols presented here may be extended to other metal bridges or ancillary ligands toward tuning the reduction potential of the central metal, improving the stability, attaching photosynthesizers or affecting the second coordination sphere.

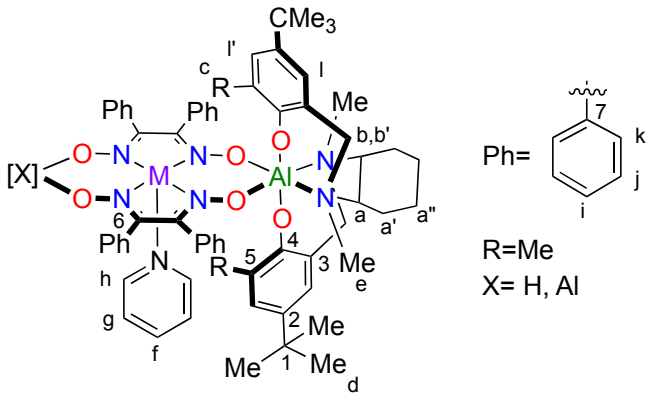
EXPERIMENTAL SECTION:

General: All air sensitive reactions were carried out in a glovebox under a nitrogen atmosphere using oven-dried glassware cooled in vacuo. Anhydrous solvents were dried by the method of Grubbs.[14] All non-dried solvents used were of reagent grade or better and were used as is. NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. C6D6 was dried over sodium/benzophnenone ketyl while CD_2Cl_2 was dried over calcium hydride, both were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. $CDCl_3$ was used as purchased. All proton NMR spectra were recorded on either a Varian Mercury 300MHz or a Varian INOVA-500 spectrometer with chemical shifts reported in ppm relative to the pertinent solvent peaks (7.16 ppm for C_6D_6, 7.26 ppm for $CDCl_3$, and 5.32 ppm for CD_2Cl_2). (R,R)-1,2-diaminocyclohexane was purified from a racemic mixture of 1,2-diaminocyclohexane using a literature procedure.[15] 2-(chloromethyl)-6-methyl-4-nitrophenol,[16a] N,N'-dimethylcyclohexane-1,2-diamine,[16b] **30**^{tBu},[11] **30**^{NO2},[11] **32**^{tBu},[11] **32**^{NO2},[11] **34**,[17] and **31 macrocycle**[11] were synthesized according to literature procedures. All other starting materials were used as purchased.

Electrochemical measurements were recorded in a glovebox under a N_2 atmosphere using a Pine Instrument Company Bipotentiostat, at 1mM of the complex of interest unless otherwise stated, in a mixture of 1:1 DCM:MeCN or DMF containing 0.1 M $nBu_4N(ClO_4)$ as the supporting electrolyte, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a 0.01M $Ag/AgNO_3$ nonaqueous reference electrode. For proton reduction trichloroacetic acid and p-cyanoanilinium triflate were used as the proton sources. Bulk electrolysis experiments were conducted in a sealed two-chambered cell where the first chamber held the working and reference electrodes and the second chamber contained the auxiliary electrode. The two chambers were separated by a fine frit.

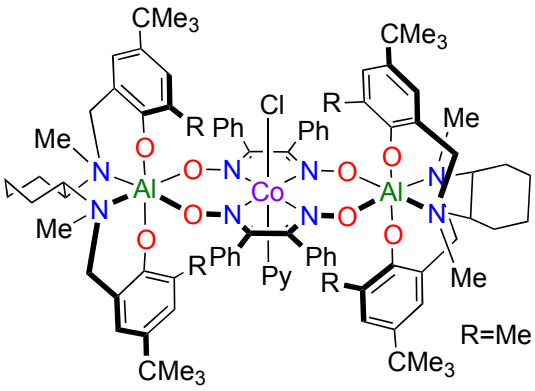
Glassy carbon plates (12 cm x 3 cm x 1 cm) were used as the working and auxiliary electrodes and submerged such that ca. 64 cm^2 of the plate was in the 0.1 M $nBu_4N(ClO_4)$ MeCN:DCM solution. For the bulk electrolysis studies para-cyanoanilinium triflate was used as the proton source. The amount of H_2 evolved was quantified from an analysis of the headspace of the cell with an Agilent 7890A gas chromotograph using a thermal conductivity detector. The overpotentials were determined by comparing the derivative of the catalytic wave observed with the stated catalyst in 3 mM trichloroacetic acid with the determined thermodynamic half wave potential of trichloroacetic acid in DMF. The thermodynamic half wave potential of trichloroacetic was determined to be -710 ± 20 mV by analysis of the catalytic wave for proton reduction in a 1M solution of trichloroacetic acid in a hydrogen (1 atm) saturated DMF solution.

Position labels for listed nuclear magnetic resonace spectroscopy characterization.



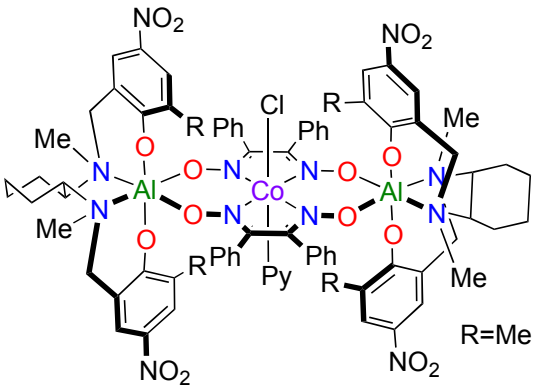
Synthesis of 35: Cobalt(III) diphenylglyoximato precursor **34** (0.127 g, 0.195 mmol) was treated with one equivalent of **31**^{tBu} (0.102 g, 0.192 mmol) in toluene (10 mL) at room temperature for 16 hours. Over time the solution became a homogeneous dark brown. The solvent was removed in vacuo resulting in a brown solid. The solid was washed with diethyl ether and extracted with benzene. The benzene solution was concentrated until solid precipitated was and filtered through celite. The filtrate was concentrated under

vacuum. To the resulting brown powder was added a small amount of benzene to barely dissolve the solid and the solution was filtered. The solvent was removed and the resulting solid was washed three times with pentane resulting in a light brown powder. Yield: 0.177 g, 79%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 19.20 (1H, s, OH), 9.13 (2H, d, J = 5.0 Hz, h), 7.75 (1H, t, J = 7.6 Hz, f), 7.29 (8H, m, j), 7.24 (2H, m, l) 7.26 (8H, m, k), 7.21 (2H, m, g), 7.16 (2H, m, i), 7.05 (2H, m, i), 6.97 (2H, d, J = 2.6 Hz, l,l'), 6.77 (2H, d, J = 2.5 Hz, l,l'), 6.50 (2H, d, J = 2.5 Hz, l,l'), 4.32 (1H, d, J = 13.4 Hz, b,b'), 3.89 (1H, d, J = 13.3 Hz, b,b'), 2.94 (1H, d, J = 13.6 Hz, b,b'), 2.75 (1H, d, J = 13.5 Hz, b,b'), 2.49 (2H, m, a), 2.12 (3H, s, e,e'), 2.07 (3H, s, e,e'), 1.85 (3H, s, c,c'), 1.66 (3H, s, c,c'), 1.63 (2H, m, a'), 1.52 (2H, m, a''), 1.35 (9H, s, d,d'), 1.25 (9H, s, d,d'), 0.96 (2H, m, a'), 0.75 (2H, m, a'') ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 157.16 (4,4'), 157.07 (4,4'), 155.40 (6,6'), 154.31 (6,6'), 153.27 (h), 139.22 (g), 136.96 (2,2'), 135.62 (2,2'), 132.56 (i,i'), 132.36 (i,i'), 130.93 (i,i'), 130.80 (i,i'), 130.03 (k,k'), 129.97 (k,k'), 129.52 (7,7'), 129.43 (7,7'), 129.11 (7,7'), 129.02 (7,7'), 128.32 (l'), 128.17 (j), 127.54 (5,5'), 126.91 (l'), 125.87 (f), 124.98 (5,5'), 123.69 (l), 123.04 (l), 121.24 (3,3'), 119.64 (3,3'), 59.86 (b,b'), 59.57 (b,b'), 55.93 (a), 55.75 (a), 40.56 (c,c'), 40.44 (c,c'), 33.97 (1), 33.76 (1), 31.96 (d), 24.62 (a"), 22.02 (a'), 17.94 (e,e'), 17.32 (e,e') ppm. Anal. Calcd. for $C_{60}H_{69}AlClCoN_6O_6$ (%): C, 66.69; H, 6.37; N, 8.38; Found: C, 67.04; H, 6.77; N, 7.99.



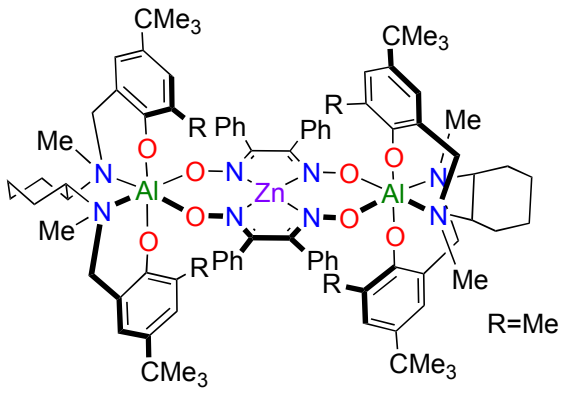
Synthesis of 36^{tBu}: A slurry of **34** (0.453 g, 0.695 mmol) in toluene (10 mL) was treated with a solution of **31^{tBu}** (0.750 g, 1.40 mmol) in toluene (10 mL) at room temperature. After 36 hours of stirring volatile materials were removed in vacuo. The crude solid was washed with hexanes. The desired product was extracted with diethyl ether and toluene. The desired product was isolated as a brown orange powder upon removing volatile material from the diethyl ether fraction. Yield: 0.437 g, 37% ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.64 (2H, d, J = 5.7 Hz, h), 7.56 (1H, t, J = 7.6 Hz, f), 7.30 (8H, m, k), 7.19 (8H, q, J = 7.8, 6.3 Hz, j), 7.13 (2H, d, J = 2.6 Hz, l'), 6.97 (2H, d, J = 2.7 Hz, l'), 6.88 (4H, d, i), 6.82 (2H, m, g), 6.64 (4H, dd, J = 12.3, 2.7 Hz, l), 4.23 (2H, d, J = 13.3 Hz, b,b'), 4.06 (2H, d, J = 13.3 Hz, b,b'), 2.90 (2H, d, J = 13.5 Hz, b,b'), 2.80 (2H, d, J = 13.5 Hz, b,b'), 2.61 (2H, m, a), 2.52 (2H, m, a), 2.26 (6H, s, e,e'), 2.21 (6H, s, e,e'), 1.84 (6H, s, c,c'), 1.66 (6H, s, c,c'), 1.60 (2H, m, a'), 1.52 (2H, m, a''), 1.29 (18H, s, d,d'), 1.28 (18H, s, d,d'), 0.96 (2H, m, a'), 0.76 (2H, m, a'') ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 157.62 (4,4'), 157.10 (4,4'), 156.05 (6,6'), 154.89 (h), 154.38 (6,6'), 138.80 (g), 136.55 (2,2'), 135.00 (2,2'), 133.66 (7,7'), 133.12 (7,7'), 130.31 (k), 130.00 (i), 128.57 (l',l'), 128.49 (l',l'), 128.04 (j,j'), 127.90 (j,j'), 127.24 (5,5'), 126.91 (l,l), 125.16 (5,5'), 124.65 (f), 123.42 (l,l), 121.05 (3,3'), 119.30 (3,3'), 60.29 (b,b'), 59.39 (b,b'), 55.88 (a), 40.57 (c,c'), 33.90 (1), 32.01 (d), 24.69 (a''), 22.08 (a'), 18.14 (e,e'),

17.42 (e,e') ppm. Elemental Analysis $C_{97}H_{121}Al_2ClCoN_9O_8$ (%): Calc. C, 68.96; H, 7.22; N, 7.46; Found. C, 69.41; H, 7.09; N, 7.15



Synthesis of 36^{NO2}: A solution of 31^{NO2} (0.111 g, 0.217 mmol) in THF (5 mL) was mixed with a solution of **3** (0.063 g, 0.090 mmol) in THF (5 mL). The mixture was sealed in a Schlenk tube and heated to 66 °C for 12 hours. After the allocated time the solvent was removed in vacuo. The recovered solid was washed with diethyl ether, benzene, and extracted with THF. The product of the THF fraction was recrystallized from a vapor diffusion of diethyl ether into THF at room temperature as brown orange crystals. The ^{1}H NMR spectrum indicates the presence of an impurity that was assigned as a isomer based on its spectroscopic features. Yield: 0.063 g, 43% ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.23 (2H, d, J = 5.1 Hz, h), 8.12 (2H, d, J = 2.9 Hz, l,l'), 7.94 (2H, d, J = 2.9 Hz, l,l'), 7.76 (4H, dd, J = 4.7, 3.0 Hz, j), 7.69 (1H, m, f), 7.41 (4H, m, j), 7.29 (2H, m, i), 7.22 (4H, dd, J = 8.3, 7.2 Hz, k), 7.17 (4H, m, k), 6.86 (2H, m, i), 6.76 (4H, d, J = 7.6 Hz, l,l'), 4.31 (2H, d, J = 13.7 Hz, b,b'), 4.17 (2H, d, J = 13.8 Hz, b,b'), 3.11 (2H, d, J = 13.9 Hz, b,b'), 3.00 (2H, d, J = 14.1 Hz, b,b'), 2.45 (2H, m, a), 2.25 (6H, s, e), 2.17 (6H, s, e), 1.80 (6H, s, c,c'), 1.70 (4H, m, a'), 1.61 (4H, m, a"), 1.54 (6H, s, c,c'), 0.95 (4H, m, a"), 0.80 (4H, m, a') ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 166.95 (4,4'), 166.24 (4,4'), 157.45 (6,6'), 156.34 (6,6'), 153.55 (h), 139.68 (f), 136.68 (2,2'), 135.82 (2,2'), 133.03 (7,7'), 131.54 (7,7'), 129.62 (k), 129.42

(i,i'), 129.33 (5,5'), 129.06 (i,i'), 128.69 (l,l'), 128.22 (l,l'), 127.29 (l,l'), 126.85 (l,l'), 126.26 (5,5'), 125.21 (g), 124.15 (j), 121.59 (3,3'), 120.09 (3,3'), 58.99 (b,b'), 58.30 (b,b'), 56.69 (a), 40.58 (c,c'), 24.41 (a"), 22.12 (a'), 17.74 (e,e'), 16.70 (e,e') ppm. Anal. Calc. $C_{81}H_{85}Al_2ClCoN_{13}O_{16}$ (%): C, 59.14; H, 5.21; N, 11.07; Found. C, 60.03; H, 5.56; N, 10.82.



Synthesis of 37: To a just thawed solution of 31^{tBu} macrocycle (0.424 g, 0.28 mmol) in THF (10 mL) was added a freshly thawed solution of diethylzinc (0.034 g, 28.6 µl, 0.28 mmol) in THF (5 mL). The solution was allowed to warm to room temperature. After 3 hours of stirring volatile materials were removed in vacuo. The crude solid was triterated with Et_2O. The resulting solid was fractionated into hexanes and THF. Removal of volatile materials from the hexanes fraction under vacuum resulted in the desired product as an off white solid. Yield 0.305 g, 69%, ^{1}H NMR (300 MHz, C6D6) δ 7.51 (8H, d, J = 7.0 Hz, k), 6.96 (16H, m, i, j, l,l'), 6.66 (4H, d, J = 2.3 Hz, l,l'), 4.59 (4H, d, J = 12.7 Hz, b,b'), 2.72 (4H, d, J = 12.7 Hz, b,b'), 2.37 (4H, m, a), 2.31 (12H, s, e), 1.91 (12H, s, c), 1.35 (36H, s, d), 1.18 (4H, m, a"), 1.04 (4H, m, a'), 0.35 (4H, m, a"), 0.26 (4H, m, a') ppm. ^{13}C{^{1}H} NMR (126 MHz, C6D6) δ 157.80 (4), 150.92 (6), 137.65 (7), 132.79 (2), 130.97 (k), 127.61 (i), 127.52 (j), 126.95 (5), 123.75 (l), 121.90 (3), 59.94 (b,b'), 55.92 (a), 39.63 (c), 33.91 (1), 32.30 (d), 24.41 (a'), 22.33 (a"), 17.78 (e) ppm. Elemental Analysis $C_{92}H_{116}Al_2ZnN_8O_8$ (%): Calc. C, 69.88; H, 7.39; N, 7.09; Found. C, 69.90; H, 7.24; N, 7.44

Acid stability test of *35*: A solution of ***35*** (0.012 g, 0.010 mmol) in C_6D_6 was mixed with (0.040 g, 0.149 mmol) trichloroacetic acid in a J-Young tube. The tube was sealed under N_2. The degradation of ***35*** was observed over time by ^{1}H NMR spectroscopy. The amount of degradation of complex was estimated from the comparison of the benzylic protons with peaks from the degradation product in the benzylic region.

Table 6.X. Crystal and refinement data for complexes **35**, **36^{tBu}**, and **36^{NO2}**.

	35	**36^{tBu}**	**36^{NO2}**
CCDC Number	861068	863680	862110
Empirical formula	$C_{65}H_{74}ClN_7O_6AlCo \cdot C_5H_{12}$	$C_{97}H_{121}N_9O_8Al_2ClCo \cdot 1.55(C_5H_{12}) \cdot 0.45(C_6H_6)$	$C_{81}H_{84}N_{13}O_{16}Al_2ClCo$
Formula weight	1242.82	1836.69	1643.95
T (K)			
a, Å	18.2062(9)	33.3885(19)	11.8585(5)
b, Å	18.3182(9)	12.4645(7)	19.9092(8)
c, Å	20.2299(10)	26.8733(15)	22.2150(9)
, deg	90	90	90
, deg	90	111.652(3)	92.687(2)
, deg	90	90	90
Volume, Å^3	6746.8(6)	10394.8(10)	5239.0(4)
Z	4	4	2
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P $2_12_12_1$	C 2	P 2_1
d_{calc}, Mg/m^3	1.224	1.174	1.042
range, deg	2.31 to 27.65°	2.31 to 27.65°	2.17 to 28.85°
μ, mm^{-1}	0.362	0.266	0.264
Abs. Correction	None	None	None
GOF	3.590	3.008	2.457
R_1,[a] wR_2[b] [I>2(I)]	R1 = 0.0610 *w*R2 = 0.0704	R1 = 0.0671 *w*R2 = 0.1146	R1 = 0.0637 *w*R2 = 0.1021

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

References

[1] a) H. B. Gray, *Nat. Chem.* **2009**, *1*, 7; b) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729-15735; c) P. Du, R. Eisenberg, *Energy Environ. Sci.* **2012**; d) V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* **2011**, *50*, 7238-7266.

[2] a) M. Frey, *ChemBioChem* **2002**, *3*, 153-160; b) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.* **2007**, *107*, 4273-4303; c) M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* **2000**, *206*, 533-561.

[3] a) G. A. N. Felton, C. A. Mebi, B. J. Petro, A. K. Vannucci, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Organomet. Chem.* **2009**, *694*, 2681-2699; b) C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245-2274.

[4] a) M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science* **2011**, *333*, 863-866; b) M. Rakowski DuBois, D. L. DuBois, *Chem. Soc. Rev.* **2009**, *38*, 62-72; c) M. Rakowski Dubois, D. L. Dubois, *Acc. Chem. Res.* **2009**, *42*, 1974-1982.

[5] a) P. Connolly, J. H. Espenson, *Inorg. Chem.* **1986**, *25*, 2684-2688; b) C. Baffert, V. Artero, M. Fontecave, *Inorg. Chem.* **2007**, *46*, 1817-1824; c) P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20627-20632; d) J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Acc. Chem. Res.* **2009**, *42*, 1995-2004; e) X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 8988-8998; f) T. Lazarides, T. McCormick, P. W. Du, G. G. Luo, B. Lindley, R. Eisenberg, *J. Am. Chem. Soc.* **2009**, *131*, 9192-9124; g) C. N. Valdez, J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15589-15593; h) F. Lakadamyali, M. Kato, N. M. Muresan, E. Reisner, *Angew. Chem. Int. Ed.* **2012**, *51*, 9381-9384; i) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem.-Int. Edit.* **2008**, *47*, 564-567; j) B. D. Stubbert, J. C. Peters, H. B. Gray, *J. Am. Chem. Soc.* **2011**, *133*, 18070-18073; k) N. K. Szymczak, L. A. Berben, J. C. Peters, *Chem. Commun.* **2009**, 6729-6731; l) L. A. Berben, J. C. Peters, *Chem. Commun.* **2010**, *46*, 398-400; m) J. P. Bigi, T. E. Hanna, W. H. Harman, A. Chang, C. J. Chang, *Chem. Commun.* **2010**, *46*, 958-960; n) Y. Sun, J. P. Bigi, N. A. Piro, M. L. Tang, J. R. Long, C. J. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 9212-9215; o) D. K. Dogutan, R. McGuire, D. G. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 9178-9180; p) C. C. L. McCrory, C. Uyeda, J. C. Peters, *J. Am. Chem. Soc.* **2012**, *134*, 3164-3170; q) S. C. Marinescu, J. R. Winkler, H. B. Gray, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15127-15131 r) M. Guttentag, A. Rodenberg, C. Bachmann, A. Senn, P. Hamm, R. Alberto, *Dalton Trans.* **2013**, *42*, 334-337; s) E. S. Andreiadis, P.-A. Jacques, P. D. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pécaut, S. Palacin, M. Fontecave, V. Artero, *Nat Chem* **2013**, *5*, 48-53.

[6] a) X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis, J. C. Peters, *Chem. Commun.* **2005**, 4723-4725; b) M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.* **2005**, *44*, 4786-4795; c) J. L. Dempsey, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2009**, *132*, 1060-1065; d) J. L. Dempsey, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2010**, *132*, 16774-16776; e) A. Fihri, V. Artero, A. Pereira, M. Fontecave, *Dalton Trans.* **2008**, 5567-5569; f) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem. Int. Ed.* **2008**, *47*, 564-567; g) P. W. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 12576-12577; h) P. W. Du, J. Schneider, G. G. Luo, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 4952-4962; i) E.

Szajna-Fuller, A. Bakac, *Eur. J. Inorg. Chem.* **2010**, 2488-2494; j) V. Artero, M. Fontecave, *Coord. Chem. Rev.* **2005**, *249*, 1518-1535; k) D. M. Cropek, A. Metz, A. M. Muller, H. B. Gray, T. Horne, D. C. Horton, O. Poluektov, D. M. Tiede, R. T. Weber, W. L. Jarrett, J. D. Phillips, A. A. Holder, *Dalton Trans.* **2012**, *41*, 13060-13073; l) P. Zhang, P.-A. Jacques, M. Chavarot-Kerlidou, M. Wang, L. Sun, M. Fontecave, V. Artero, *Inorg. Chem.* **2012**, *51*, 2115-2120.

[7] a) B. H. Solis, S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2011**, *133*, 19036-19039; b) T. M. McCormick, Z. J. Han, D. J. Weinberg, W. W. Brennessel, P. L. Holland, R. Eisenberg, *Inorg. Chem.* **2011**, *50*, 10660-10666.

[8] a) A. Yeori, I. Goldberg, M. Shuster, M. Kol, *J. Am. Chem. Soc.* **2006**, *128*, 13062-13063; b) Y.-L. Wong, Y. Yan, E. S. H. Chan, Q. Yang, T. C. W. Mak, D. K. P. Ng, *J. Chem. Soc., Dalton Trans.* **1998**, 3057-3064; c) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen, J. Feijen, *Chem. Eur. J.* **2009**, *15*, 9836-9845.

[9] a) C. López, S. Alvarez, M. Aguiló, X. Solans, M. Font-Altaba, *Inorg. Chim. Acta* **1987**, *127*, 153-159; b) K. A. Lance, W.-K. Lin, D. H. Busch, *Acta Crystallogr. Sect. C: Commun. Online* **1991**, *C47*, 1401-1403.

[10] a) J. L. Hoard, *Science* **1971**, *174*, 1295-1302; b) K. M. Kadish, K. M. Smith, R. Guilard, *Porphyrin Handbook* **2000**, *1*.

[11] P. Kelley, M. R. Radlauer, A. J. Yanez, M. W. Day, T. Agapie, *Dalton Trans.* **2012**, *41*, 8086-8092.

[12] a) D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll, S. N. Brown, *Inorg. Chem.* **2010**, *49*, 4687-4697; b) B. Adam, E. Bill, E. Bothe, B. Goerdt, G. Haselhorst, K. Hildenbrand, A. Sokolowski, S. Steenken, T. Weyhermüller, K. Wieghardt, *Chem. Eur. J.* **1997**, *3*, 308-319.

[13] a) G. A. N. Felton, R. S. Glass, D. L. Lichtenberger, D. H. Evans, *Inorg. Chem.* **2006**, *45*, 9181-9184; b) V. Fourmond, P.-A. Jacques, M. Fontecave, V. Artero, *Inorg. Chem.* **2010**, *49*, 10338-10347.

[14] a) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics.* **1996**, *15*, 1518-1520

[15] J. F. Larrow, E. N. Jacobson, Y. Gao, Y. Hong, X. Nie, C. M. Zepp, *J. Org. Chem.* **1994**, *59*, 1939-1942.

[16] a) C. A. Buehler, F. K. Kirchner, G. F. Deebel, *Organic Synthesis* **1955**, *3*, 468; b)V. Stepanenko, M. De Jesús, W. Correa, I. Guzmán, C. Vázquez, L. Ortiz, M. Ortiz-Marciales, *Tetrahedron: Asymmetry* **2007**, *18*, 2738-2745.

[17] G. N. Schrauzer, *Inorganic Synthesis* **1968**, *11*, 62-64.