Synthetic and Structural Studies of Mono-acetylide and Unsymmetric Bis-acetylide Complexes based on Co^{III}-cyclam

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Abstract: Reported in this contribution are the synthesis and characterization of both mono-acetylide and unsymmetric bis-acetylide compounds based on Co^{III}(cyclam) (cyclam = 1,4,8,11-tetraazacyclotetradecane). Refluxing [Co(cyclam)Cl₂]Cl with HC₂R in the presence of organic amine resulted in the formation of *trans*-[Co(cyclam)(C₂R)Cl]Cl (R = -4-C₆H₄NO₂ (**1a**), -ferrocenyl (**1b**) and -4-C₆H₄SC₂H₄SiMe₃ (**1c**)) in satisfactory yields. Subsequent reactions between LiC₂Ph and *trans*-[Co(cyclam)(C₂-4-C₆H₄NO₂)Cl]Cl resulted in a mixture of *trans*-[Co(cyclam)(C₂-4-C₆H₄NO₂)(C₂Ph)]Cl (**2a**) and *trans*-[Co(cyclam)(C₂Ph)₂]Cl (trace). Molecular structures of the new compounds were established using single crystal X-ray diffraction. Cyclic voltammetric study revealed that these compounds typically display three Co-based couples: an irreversible 1e⁻ oxidation, and two 1e⁻ reductions.

1. Introduction

There has been a long standing interest in the synthesis and physical properties of metal acetylide complexes [1,2], and the recent decades have witnessed much of activity in using metal acetylides as the building blocks for molecular wires [3-9], non-linear optical chromophores [10,11], and photovoltaic materials [12,13]. Examples of metal acetylides exhibiting extensive conjugation, a prerequisite for molecular wires, include those based on Fe [14,15], Ru [16-18], Re [19,20] and Ru₂ [21-26]. Though less frequent, reports of metal acetylides functioning as molecular wires or active materials in devices have also appeared in literatures in recent years [27-33]. In addition to the aforementioned study of Ru₂-based acetylides, our laboratory has investigated a number of M^{III}-cyclam (M = Cr, Fe and Co; cyclam = 1,4,8,11-tetraazacyclotetradecane) based acetylide complexes, and elucidated their structural and voltammetric properties [34-37]. It should be noted that other laboratories have also explored the acetylide chemistry of M^{III}-cyclam complexes [38-43]. While the majority of the M^{III}-cyclam acetylides are the symmetric *trans*-[M(cyclam)(C₂R)₂]⁺ type obtained using lithium acetylide, a unique Co^{III} species, *trans*-[Co(cyclam)(C₂Ph)Cl]⁺, was prepared using the weak-base assisted alkynylation method by the laboratory of Shores [44]. Subsequently, our laboratory reported that treating [Co(cyclam)Cl₂]Cl with *ca.* 0.5 equiv of Me₃SiC_{2n}SiMe₃ in the presence of weak base resulted in novel oligoyn-diyl bridged compounds *trans*-{[Co(cyclam)Cl]₂(μ-C_{2n})²⁺ with *n* = 2 and 3 [45].

In addition to functioning as electronic wires, metal acetylides can also serve as photonic wires. Recently, Weinstein *et al.* reported that the photo-induced electron transfer within a donor-bridge-acceptor diad (D-B-A) is modulated by selective excitation of C≡C vibration of the *trans*-C≡C-Pt-C≡C bridge [46,47]. This elegant example inspired us to consider similar D-B-A

constructs based on *trans*-[M(cyclam)(C≡C-)₂] bridges, which have the advantage of using earth abundant 3d metals. The aforementioned work on Co system is an ideal starting point because of the highly selective formation of *trans*-[Co(cyclam)(C₂R)Cl]⁺ [44]. As the first step towards M(cyclam)-based D-B-A diad, we report herein the synthesis and characterization of new *trans*-[Co(cyclam)(C₂R)Cl]⁺ type compounds (**1a/b/c** in Scheme 1) and an unsymmetric compound *trans*-[Co(cyclam)(C₂Ph)(C₂C₆H₄-4-NO₂)]⁺ (**2a**).

Scheme 1. Synthesis of mono- and bis-acetylide Co(cyclam) Compounds

Conditions: (i) 1 equiv HC₂R, base (excess), MeOH reflux 12 h;
(ii) 1.0 equiv LiC₂Ph, THF; 8 h; Counter ion is chloride in all cases

2. Results and Discussion

2.1. Synthesis

Compounds **1a/b/c** were prepared by refluxing a methanolic solution of [Co(cyclam)Cl₂]Cl and HC₂R in the presence of an organic amine overnight. Though the alkynylation did not proceed to 100% completion, the desired product can be readily separated from the residue [Co(cyclam)Cl₂]Cl on a silica column. The nature of organic base also has a subtle role: triethylamine worked very well for the preparation of both **1a** and **1c** while

diethylamine led to a much higher yield for **1b**. Compounds **1a/b/c** were isolated in satisfactory yields of 50 – 70%, which are comparable to those reported for [Co(cyclam)(C₂Ph)Cl](BPh₄), {[Co(cyclam)Cl]₂(μ-*p*-DEB)}(BPh₄)₂ and {[Co(cyclam)Cl]₃(μ-1,3,5-TEB)}(BPh₄)₃ by Shores *et al.* (DEB and TEB are diethynylbenzene and triethynylbenzene, respectively) [44].

The introduction of the second acetylide ligand was achieved through the reaction between **1a** and lithiated phenylacetylene as shown in Scheme 2. Reactions between **1a** and one equiv of LiC₂Ph yielded compound **2a** (22%). A major limitation of such approach is that while the substitution of the chloro ligand is the primary reaction, acetylide metathesis also occurs as evidenced by the detection of [Co(cyclam)(C₂Ph)₂]⁺ [in the reaction](#).

Consistent with the Co^{III} center being a low spin *d*⁶ ion, all compounds reported here are diamagnetic and hence can be characterized by ¹H NMR spectroscopy. In addition, all compounds have been characterized by ESI-MS and combustion analysis with satisfactory results.

2.2. X-ray and molecular structures of **1a**, **1b**, **1c** and **2a**.

Both the mono- and bis-acetylide compounds were readily crystallized from slow diffusion of a less polar solvent (ether or hexanes) into their methanol or methylene chloride solutions. Molecular structures of compounds **1a**, **1b**, **1c** and **2a** were determined using single crystal X-ray diffraction, and the structural plots of the cations are shown in Figures 1, 2, 3 and 4, respectively. Selected bond lengths and angles are collected in Table 1, while the relevant crystal data are provided in Table 3 at the end of the *Experimental* section.

Figure 1. ORTEP plot of compound **1a**⁺ at 30% probability level. Hydrogen atoms were omitted for clarity.

The Co^{III} coordination spheres in **1a**⁺, **1b**⁺ and **1c**⁺ are all pseudo-octahedral, and similar to those reported for [Co(cyclam)(C₂Ph)Cl]⁺ [44] and {[Co(cyclam)Cl]₂(μ-C_{2n})}²⁺ [45]. The cyclam ligands exhibit very comparable ring conformations, and the Co-N bond lengths in Table 1 are within a narrow range of 1.962 – 1.987 Å. Adhering to the pseudo-octahedral geometry, both the C-Co-Cl angles in **1**⁺ and the C-Co-C angle in **2a**⁺ are all nearly linear. Among the mono-acetylide species, the Co-C bond lengths are in the order of **1a**⁺ ~ **1c**⁺ < **1b**⁺. Given the fact that *p*-nitrophenylacetylide is the least electron donating of the three, the order of bond lengths is unlikely related solely to the σ-donor strength. It is likely that the Co-C≡C π interactions also play a significant role here. It is established that the π interactions between a transition metal center and σ-acetylide ligand are dominated by the filled-filled antibonding type [48,49]. The *p*-nitro group acts as a strong π-acceptor, which pulls the π(C≡C) electron density away from metal center, and hence significantly reduces the antibonding π interaction between the Co center and C≡C bond. Although ferrocenyl is more electron donating than aryls, the π(C≡C) of FcC₂ ligand has probably the strongest antibonding interaction with *d*π(Co) and hence the longest Co-C bond

for **1b**⁺. The Co-C bond length in {[Co(cyclam)Cl]₂(μ-C₈)}²⁺ (1.874(3) Å) is slightly shorter than that in **1c**⁺ due to a high degree of electron deficiency in an oligoyn-diyl chain [45].

Figure 2. ORTEP plot of compound **1b**⁺ at 30% probability level. Hydrogen atoms were omitted for clarity.

Figure 3. ORTEP plot of compound **1c**⁺ at 30% probability level. Hydrogen atoms were omitted for clarity.

Molecular structures of symmetric bis-acetylide compounds, namely [Co(cyclam)(C₂R)₂]⁺, have been reported for R = Ph by Shores [44] and R = CF₃ by Wagenknecht [41]. Though the coordination sphere of **2a**⁺ is very similar to those of [Co(cyclam)(C₂Ph)₂]⁺ and [Co(cyclam)(C₂CF₃)₂]⁺, the molecular structure is unique owing to its asymmetry. Interestingly, the trend of the Co-C distances is [Co(cyclam)(C₂CF₃)₂]⁺ (1.917) < **2a**⁺ (1.924 and 1.991) < [Co(cyclam)(C₂Ph)₂]⁺ (2.001), which parallels the influence of the acetylide ligands on the electron richness of the Co^{III} center. Furthermore, the Co-

C(nitrophenylacetylene) bond length of $\mathbf{2a}^+$ is slightly longer than that of $[\text{Co}(\text{cyclam})(\text{C}_2\text{CF}_3)_2]^+$, while the Co-C(phenylacetylene) bond length of $\mathbf{2a}^+$ is slightly shorter than that of $[\text{Co}(\text{cyclam})(\text{C}_2\text{Ph})_2]^+$. The shortness of Co-C in $[\text{Co}(\text{cyclam})(\text{C}_2\text{CF}_3)_2]^+$ was previously attributed to a weak π -acidity of $-\text{C}_2\text{CF}_3$ ligand [41]. However, our DFT calculations on related Co^{III} acetylides generally place $\pi^*(\text{C}\equiv\text{C})$ significantly above Co $d\pi$ orbitals [37,45], which makes the former an unlikely acceptor. It is more likely that the electron withdrawing ability of $-\text{CF}_3$ and $-\text{C}_6\text{H}_4-4-\text{NO}_2$ significantly reduces the antibonding contribution from $\pi(\text{C}\equiv\text{C})$ to Co $d\pi$, and hence strengthens the Co-C bond. Also noteworthy is that both Co-C bonds in $\mathbf{2a}^+$ are significantly longer than those in compounds $\mathbf{1}^+$. This is because the acetylide is a much stronger donor than the chloro, and both acetylides in $\mathbf{2a}^+$ experience the *trans*-influence of each other.

Figure 4. ORTEP plot of compound $\mathbf{2a}^+$ at 30% probability level. Hydrogen atoms were omitted for clarity.

Table 1: Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for $\mathbf{1a}^+$, $\mathbf{1b}^+$, $\mathbf{1c}^+$ and $\mathbf{2a}^+$

	$\mathbf{1a}^+$	$\mathbf{1b}^+$	$\mathbf{1c}^+$	$\mathbf{2a}^+$
Co1-C1	1.877(4)	1.883(2)	1.879(2)	1.924(4)
Co1-C3	--	--	--	1.991(4)
Co1-N1	1.982(4)	1.985(2)	1.970(2)	1.977(4)
Co1-N2	1.976(4)	1.962(2)	1.974(2)	1.991(3)

Co1-N3	1.966(4)	1.970(2)	1.976(2)	1.977(4)
Co1-N4	1.987(4)	1.985(2)	1.972(2)	1.978(3)
Co1-C11	2.312(1)	2.3226(6)	2.3185(6)	--
C1-C2	1.215(6)	1.209(3)	1.210(3)	1.214(5)
C3-C4	--	--	--	1.157(5)
C11-Co1-C1	177.7(1)	178.42(7)	178.18(7)	--
C3-Co1-C1	--	--	--	177.6(1)
Co1-C1-C2	168.2(4)	173.8(2)	176.9(2)	170.1(3)
C1-C2-C3	176.0(5)	177.1(2)	175.3(3)	--
C1-C2-C11	--	--	--	179.3(5)
Co1-C3-C4	--	--	--	173.9(4)
C3-C4-C5	--	--	--	177.7(5)

2.3. Spectroscopic studies

The electronic absorption spectra of both compounds **1** and **2** feature a weak band ($\epsilon \sim 10^2$) in the visible window and an intense band ($\epsilon \sim 10^4$) in the UV window, as exemplified by the spectra of **1a** and **2a** in Figure 5. The spectral features of **1b** and **1c** are very similar to that of **1a**. The lower energy transitions, peaks at 478 nm for **1a** and 442 nm for **2a**, are likely attributed to the ligand field (*d-d*) transition $^1A_{1g} \rightarrow ^1T_{1g}$, according to the discussion by Wagenknecht for the symmetric $[\text{Co}(\text{cyclam})(\text{C}_2\text{R})_2]^+$ type compounds [41]. Wagenknecht also noted that the intensities of *d-d* bands for $[\text{Co}(\text{cyclam})(\text{C}_2\text{R})_2]^+$ are about three times of that for $[\text{Co}(\text{cyclam})(\text{CN})_2]^+$ because of more efficient intensity stealing from the high energy CT band. Interestingly, the *d-d* band of **2a** is further intensified by at least three fold in comparison with those of $[\text{Co}(\text{cyclam})(\text{C}_2\text{R})_2]^+$ ($\epsilon \sim 150$ or less), likely the result of the electronic asymmetry

(thus a permanent dipole) along the $\text{PhC}_2\text{-Co-C}_2\text{C}_6\text{H}_4\text{-NO}_2$ axis. The higher energy transitions, peaks at 337 nm for **1a** and 270 nm for **2a**, are likely the LMCT transitions from axial chloro / acetylide ligands [39]. The intensity of the LMCT band of **2a** is significantly lower than that of **1a**, implying a prominent contribution from the chloro ligand in the latter.

Figure 5. UV-Vis spectra of compounds **1a** and **2a** recorded in methanol solution. The inset is the enlargement of the visible region.

Figure 6. Cyclic voltammograms of compounds **1a**, **1b** and **2a** recorded in 0.10 M Bu₄NBF₄ acetonitrile solution with a scan rate of 100 mV/s. Description for the green and blue insets in the CV of **1a** is given in the discussion below.

2.4. Electrochemistry

Compounds **1** and **2** exhibit several 1e⁻ redox couples in their cyclic voltammograms (CV), as exemplified by the CVs of **1a**, **1b** and **2a** (Figure 6). Electrode potentials determined for all of the new compounds are listed in Table 2. The CV of the mono-acetylide species **1b** consists of a reversible ferrocenyl oxidation at 0.10 V and an irreversible Co-based oxidation at 0.81 V, and irreversible Co-based reductions at -1.52 and -1.89 V. The anodic portion of the CV of **1a** has the irreversible oxidation **A** at a potential slightly more positive than that of **1b**, reflecting the increased electron deficiency due to the nitrophenyl group. **Because of the absence of current on the back sweep, the Co^{III} species is likely completely degraded passing E_{pa}(**A**) and the resultant species is labeled as “Co^{IV}” in Scheme 2.** The impact of the nitrophenyl group is more pronounced in the cathodic region: the first (**B**) and second (**C**) reductions are significantly shifted to the positive direction compared with those of **1b**. Furthermore, a substantial anodic wave was observed on the backward sweep immediately beneath the closely spaced cathodic peaks **B** and **C**. To ascertain the origin of this wave, the cathodic scans with the end point shortly past E_{pc}(**B**) (green) and E_{pc}(**C**) (blue) were performed and included in Figure 6. It is clear from these CVs that the anodic peak is associated with reduction **C** and makes the couple quasi-reversible. This observation is consistent with the prior report of the CVs for [Co(cyclam)(C₂R)₂]⁺, for which the reversibility of the Co(III/II) couple improves as R becoming more electron withdrawing [41]. Reduction of the nitro-group occurs at very negative potential and results in degradation of the Co compound, as evidenced by the broadening of the anodic peak below **C** and the appearance of a new anodic wave near 0 V when compared to the

CVs in green and blue. Based on the voltammetric results of **1b** and **1c**, a simple assignment to explain the observed couples is given in Scheme 2 below.

Scheme 2. Assignment of Co-based redox couples observed for **1** (top) and **2** (bottom); C₂R' indicates the less electron deficient acetylide.

Compound **2a** exhibits an irreversible 1e⁻ oxidation and three 1e⁻ reductions. In contrast to **1a**, it is the first 1e⁻ reduction **B** that is quasi-reversible, which is consistent with the prior report of [Co(cyclam)(C₂R)₂]⁺ [41]. As outlined in Scheme 2, the second 1e⁻ reduction is reversible because of the dissociation of the less electron deficient acetylide (-C₂Ph). The retention of the nitrophenylacetylide is also supported by the observation of the reduction of nitro group.

Table 2. Electrode potentials of all observed redox couples (V) in compounds **1** and **2**

	E _{pa} (A)	E _{pc} (B)	E _{pc} (C)	E _{1/2} (Fc)	E _{pc} (-NO ₂)
[Co(cyclam)Cl(C ₂ C ₆ H ₄ -4-NO ₂)]Cl (1a)	0.81	-1.29	-1.42	--	-2.09
[Co(cyclam)Cl(C ₂ Fc)]Cl (1b)	0.74	-1.52	-1.89	0.10	--
[Co(cyclam)Cl(C ₂ C ₆ H ₄ -4-SC ₂ H ₄ SiMe ₃)]Cl (1c)	0.81	-1.147	-1.79	--	--
[Co(cyclam)(C ₂ Ph)(C ₂ C ₆ H ₄ -4-NO ₂)]Cl (2a)	0.88	-1.41	-1.76	--	-1.95

3. Conclusion

Presented in this contribution is the general synthesis of the *trans*-[Co(cyclam)(C₂R)Cl]Cl type compounds **1a/b/c**, and facile conversion of **1a** to the unsymmetric bis-acetylide derivative *trans*-[Co(cyclam)(C₂Ph)(C₂C₆H₄-4-NO₂)]Cl (**2a**). As discussed above, the presence of *para*-nitro substituent and the unsymmetric nature of **2a** have significant

influence on both the electronic absorption spectra and voltammetric behaviors of Co(cyclam) acetylides. While the synthetic method for *trans*-[Co(cyclam)(C₂R)Cl]Cl in satisfactory yield and purity has been established, the current synthesis of the unsymmetric bis-acetylide derivative is of low yield. Preparations of unsymmetric bis-acetylides that do not involve lithium acetylides have been documented in literature: the reaction between *trans*-[(dppe)₂RuCl(C₂Ar)] and Me₃SnC₂Ar' resulted in *trans*-[(dppe)₂Ru(C₂Ar)(C₂Ar')] (dppe = 1,2-bis(diphenylphosphino)ethane) [50], and *trans*-Pt(PBu₃)₂Cl(C₂R) was converted to *trans*-Pt(PBu₃)₂(C₂R)(C₂R') under the Hagihara conditions (CuI / organic amine) [47]. More selective and higher yield methods for the *trans*-[Co(cyclam)(C₂R)(C₂R')]Cl type compounds are being sought in our laboratory.

4. Experimental

4.1. General Procedures. [Co(cyclam)Cl₂]Cl was prepared according to literature procedures [37]. Also prepared according literature procedures were ethynylferrocene [51], 4-NO₂-C₆H₄C₂SiMe₃ [52] and 4-(Me₃SiC₂H₄S)-C₆H₄C₂H [53]. THF was distilled over Na/benzophenone under a N₂ atmosphere. UV-Vis-NIR spectra were obtained with a JASCO V-670 UV-Vis-NIR spectrophotometer. Infrared spectra were obtained on a JASCO FT-IR 6300 spectrometer via ATR on a ZnSe crystal. Mass Spectrometry data were collected on a Waters 600 LC/MS. ¹H NMR spectra were recorded on a Varian MERCURY300 NMR spectrometer. Cyclic voltammograms were recorded in 0.1 M n-Bu₄NPF₆ and 1.0 mM cobalt species solution (CH₃CN, Ar degassed) by a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), Pt-wire counter electrode, and a Ag/AgNO₃ reference electrode with ferrocene used as an external reference (E_{1/2} = 0.12 V).

4.2. Preparation of *1a*. [Co(cyclam)Cl₂]Cl (220 mg, 0.54 mmol), 4-NO₂-C₆H₄C₂SiMe₃ (120 mg, 0.54 mmol), and Et₃N (4.0 mL) were mixed in 20 mL of methanol, and the mixture was refluxed overnight to yield a muddy red solution. After solvent removal, the crude mixture was loaded onto a short silica gel plug and eluted first with CH₂Cl₂, then CH₃OH/CH₂Cl₂ (v/v, 1:6). An orange and a green fraction were collected with the second eluent, and identified by ESI-MS as the desired product and the starting material, respectively. After solvent removal, the orange fraction was recrystallized from ether-methanol to afford 168 mg of **1a** (70% based on Co). When Et₂NH was used in place of Et₃N, the reaction only yielded a mixture of intractable products. Data for **1a**: ESI-MS: [M]⁺, 440.0. ¹H NMR (CD₃OD, δ): 8.175 (dd, 2H, Ph), 7.645 (dd, 2H, Ph), 5.2 (br s, 4H, NH). UV-vis spectra, λ_{max} (nm, ε (M⁻¹ cm⁻¹)): 337 (46,300), 478 (155); IR (cm⁻¹): C≡C: 2114(m). Anal. Found (calcd) for C₁₈H₃₀Cl₂CoN₅O₃ (**1a**·H₂O): C, 43.31 (43.74); H, 5.86 (6.12); N, 13.84 (14.17).

4.3. Preparation of *1b*. [Co(cyclam)Cl₂]Cl (200 mg, 0.61 mmol), ethynylferrocene (107 mg, 0.51 mmol) and Et₂NH (2.0 mL) were mixed in 10 mL of methanol, and the mixture was refluxed for overnight to yield a dark red solution. After solvent removal, the crude mixture was loaded onto a short silica gel plug and eluted with first CH₂Cl₂, then CH₃OH/CH₂Cl₂ (v/v, 1:6). Both a red and a green fraction were collected using the latter eluent, and were identified by ESI-MS as the desired product and starting materials, respectively. After solvent removal, the red fraction was recrystallized from ether-methanol to afford 162 mg of **1b** (63% based on ethynylferrocene). When Et₃N was used in place of Et₂NH, the reaction between [Co(cyclam)Cl₂]Cl and ethynylferrocene only resulted in **1b** in *ca.* 10% yield. Data for **1b**: ESI-MS: [M]⁺, 503.0. ¹H NMR (CD₃OD, δ): 4.990 (br s, 4H, NH), 4.894 (s, 2H, Fc), 4.470 (s, 2H, Fc), 4.206 (s, 5H, Fc). UV-vis spectra, λ_{max} (nm, ε (M⁻¹ cm⁻¹)): 270 (15,300), 442 (548); IR (cm⁻¹

¹): C≡C, 2132(m). Anal. Found (calcd) for C₂₃H₃₅Cl₄CoFeN₄ (**1b**·CH₂Cl₂): C, 44.01 (44.26); H, 5.65 (5.92); N, 8.81 (8.98).

4.4. Preparation of 1c. [Co(cyclam)Cl₂]Cl (110 mg, 0.41 mmol), 4-(Me₃SiC₂H₄S)-C₆H₄C₂H (110 mg, 0.47 mmol) and Et₃N (1.6 mL) were mixed in 10 mL of methanol, and the mixture was refluxed for overnight to yield a dark red solution. Solvent was removed under reduced pressure, and the crude residue was loaded onto a short silica gel plug and eluted with first CH₂Cl₂, then CH₃OH/CH₂Cl₂ (v/v, 1:6). Both a red and a green fraction were collected using the latter eluent, and were identified by ESI-MS as the desired product and starting materials, respectively. After solvent removal, the red fraction was recrystallized from ether-methanol to afford 120 mg of **1c** (52% based on Co). Data for **1c**: ESI-MS: [M]⁺, 527.0. ¹H NMR (CD₃OD, δ): 7.37 (dd, 2H, Ph), 7.23 (dd, 2H, Ph), 5.08 (br s, 4H, NH), 1.94 (m, 2H, CH₂), 1.60 (m, 2H, CH₂), 0.030 (s, 9H, TMS). UV-Vis spectra, λ_{max} (nm, ε (M⁻¹ cm⁻¹)): 285 (28,500), 491 (112); IR (cm⁻¹): C≡C: 2122(m). Anal. Found (calcd) for C₂₃H₃₇Cl₂CoN₄O₃SSi (**1c**·3H₂O): C, 44.70 (44.73); H, 7.66 (7.67); N, 8.97 (9.07)

4.5. Preparation of 2a. Under an N₂ atmosphere, LiC₂Ph in THF (0.29 mmol) was added to a Schlenk flask containing **1a** (119 mg, 0.27 mmol) in 5 mL THF, and the reaction mixture was allowed to stir overnight to yield a brown solution. After solvent removal, the crude residue was loaded onto a short silica gel plug and eluted first with EtOAc, then CH₃OH/EtOAc (v/v 1:6). Both a yellow and an orange fraction were collected using the latter eluent, and were identified by ESI-MS as the desired product and the starting material, respectively. The material from the yellow fraction was recrystallized from ether-methanol to afford 30 mg of **2a** (22% based on **1a**). Data for **2a**: ESI-MS: [M]⁺, 506.0. ¹H NMR (CD₃OD, δ): 8.17 (dd, 2H, PhNO₂), 7.65 (dd, 2H, PhNO₂), 7.47 (dd, 2H, Ph), 7.26 (dt, 2H, Ph), 7.17 (dd, 1H, Ph), 4.72 (br s, 4H, NH), UV-Vis

spectra, $\lambda_{\max}$ (nm, ϵ ($M^{-1} \text{ cm}^{-1}$)): 270 (15,300), 442 (435); IR (cm^{-1}): $\text{C}\equiv\text{C}$, 2054 (w), 2097(s).

Anal. Found (calcd) for $\text{C}_{26}\text{H}_{41}\text{ClCoN}_5\text{O}_5$ (**2a** $\cdot 2\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$): C, 53.49 (53.16); H, 6.59 (6.77); N, 11.50 (11.48).

4.6. Structure Determination: Single crystals of compound **1a**, **1b** and **2a** were grown by slow diffusion of ether into methanol at room temperature. Single crystals of **1c** were grown by slow diffusion of hexanes into dichloromethane solution at room temperature. X-ray diffraction data were collected on either a Rigaku Rapid II image plate diffractometer using Cu K α (**1a** and **2a**) or a Nonius Kappa CCD using Mo K α (**1b** and **1c**), and the structures were solved using the structure solution program PATTY in DIRDIF99 [54], and refined using SHELX-07 [55]. Crystallographic data are listed in Table3.

Table 3. Crystal data for compounds **1a**, **1b**, **1c** and **2a**

	1a $\cdot 2\text{CH}_3\text{OH}$	1b $\cdot 3\text{CH}_3\text{OH}$	1c $\cdot 2\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$	2a $\cdot 2\text{CH}_3\text{OH}$
Chemical Formula	$\text{C}_{20}\text{H}_{36}\text{Cl}_2\text{CoN}_5\text{O}_4$	$\text{C}_{25}\text{H}_{45}\text{Cl}_2\text{CoFeN}_4\text{O}_3$	$\text{C}_{25}\text{H}_{47}\text{Cl}_6\text{CoN}_4\text{OSSi}$	$\text{C}_{28}\text{H}_{41}\text{ClCoN}_5\text{O}_4$
Formula Weight	540.38	635.35	751.48	606.06
Space Group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a , Å	8.0601(6)	18.9682(5)	9.5458(7)	10.3849(8)
b , Å	10.1925(7)	11.1569(2)	13.291(1)	12.532(1)
c , Å	16.7491(9)	14.1810(3)	14.490(1)	12.705(1)
α °	92.12(5)		94.77(5)	92.40(8)
β °	93.70(6)	105.40(1)	90.69(5)	109.43(7)
γ °	104.24(5)		102.55(4)	108.92(7)
V , Å ³	1328.9(2)	2893.4(1)	1787.4(2)	1454.0(2)
Z	2	4	2	2
T , K	150	150	150	150
λ , Å	1.54184	0.71073	0.71073	1.54184
ρ_{calcd} , g cm ⁻³	1.350	1.458	1.396	1.384
R	0.061	0.037	0.040	0.058
$wR2$	0.152	0.084	0.100	0.148

5. Supporting Information Available. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 1411094 - 1411097 for compounds **1a**, **1b**, **1c** and **2a**, respectively. Copies of this information may be

obtained free of charge from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK,
(Fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>).

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