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Synthesis and Molecular and Electronic Structures of Reduced Bis(imino)pyridine Cobalt Dinitrogen Complexes: Ligand versus Metal Reduction

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Abstract: Sodium amalgam reduction of the aryl-substituted bis(imino)pyridine cobalt dihalide complexes (^{Ar}PDI)CoCl$_2$ and (^{iPr}BPDI)CoCl$_2$ (^{Ar}PDI = 2,6-(2,6-R$_2$-C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N (R = ^{i}Pr, Et, Me); ^{iPr}BPDI = 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N=CPh)$_2$C$_5$H$_3$N) in the presence of an N$_2$ atmosphere furnished the corresponding neutral cobalt dinitrogen complexes (^{Ar}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$. Magnetic measurements on these compounds establish doublet ground states. Two examples, (^{iPr}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$, were characterized by X-ray diffraction and exhibit metrical parameters consistent with one-electron chelate reduction and a Co(I) oxidation state. Accordingly, the toluene solution EPR spectrum of (^{iPr}PDI)CoN$_2$ at 23 °C exhibits an isotropic signal with a g value of 2.003 and hyperfine coupling constant of 8×10^{-4} cm^{-1} to the $I = 7/2$ ^{59}Co center, suggesting a principally bis(imino)pyridine-based SOMO. Additional one-electron reduction of (^{iPr}PDI)CoN$_2$ was accomplished by treatment with Na[C$_{10}$H$_8$] in THF and yielded the cobalt dinitrogen anion [(^{iPr}PDI)CoN$_2$]$^-$. DFT calculations on the series of cationic, neutral, and anionic bis(imino)pyridine cobalt dinitrogen compounds establish Co(I) centers in each case and a chelate-centered reduction in each of the sequential one-electron reduction steps. Frequency calculations successfully reproduce the experimentally determined N≡N infrared stretching frequencies and validate the computational methods. The electronic structures of the reduced cobalt dinitrogen complexes are evaluated in the broader context of bis(imino)pyridine base metal chemistry and the influence of the metal d electron configuration on the preference for closed-shell versus triplet diradical dianions.

Introduction

In base metal catalysis, aryl-substituted bis(imino)pyridines are a privileged class of ligands.[1,2] Brookhart and Gibson's independent discoveries of ethylene and α-olefin polymerization (oligomerization) upon treatment of [(^{Ar}PDI)MX$_2$] (^{Ar}PDI = 2,6-(2,6-R$_2$-C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N (R = ^{i}Pr, Et, Me, H, etc.); M = Fe, Co; X = Cl, Br) derivatives with excess methylaluminoxane (MAO) renewed interest in exploring the utility of classical, Werner-type coordination compounds of iron and cobalt as catalyst precursors.[3−6] Bis(imino)pyridines have also found application as supporting ligands in catalytic reactions relevant to small-molecule organic methods. Gal and co-workers have reported that square planar, aryl-substituted bis(imino)pyridine cobalt alkyl complexes (^{iPr}PDI)CoR^1 (R^1 = Me, CH$_2$Ph, CH$_2$SiMe$_3$) are precatalysts for the hydrogenation of mono- and disubstituted olefins.[7] In iron chemistry, the bis(imino)pyridine iron bis(dinitrogen) complexes (^{iPr}PDI)Fe(N$_2$)$_2$ and (^{iPr}BPDI)-Fe(N$_2$)$_2$ exhibit high activity for the hydrogenation and hydrosilylation of unactivated alkenes.[8] In addition, (^{iPr}PDI)Fe(N$_2$)$_2$ serves as a precatalyst for the hydrogenation of functionalized olefins,[9] diene [$2\pi + 2\pi$] cycloisomerization,[10] and hydrogen-mediated enyne and diyne cyclization.[11]

One distinguishing feature of bis(imino)pyridine ligands is their redox activity[12,13]—the ability to accept one to three electrons from the metal and stabilize reduced compounds whose low formal oxidation state assignment may be deceiving.[14]

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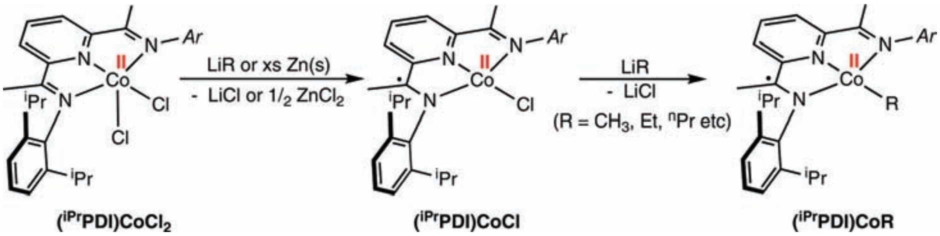
Scheme 1



Seminal electrochemical studies by Toma on bis(chelate) complexes of bis(imino)pyridine iron established the participation of these ligands in the electronic structures of reduced metal complexes.[15,16] In preparative scale chemistry, Wieghardt and co-workers synthesized bis(imino)pyridine bis(chelate) complexes of a series of first-row ions and demonstrated that redox processes occur at the ligand rather than the metal.[17,18] These studies also established many of the metrical and spectroscopic features that signal chelate participation. It is likely that the ability of the bis(imino)pyridine ligands to smoothly adjust to the electronic demands of the metal center is the reason why these ligands enable such a broad and rich catalytic chemistry.[19]

Irreversible carbon−oxygen bond cleavage has been identified as a significant catalyst deactivation pathway in alkene hydrogenation and $[2\pi + 2\pi]$ cycloisomerization reactions promoted by $(^{iPr}PDI)Fe(N_2)_2$.[20] Because of this limitation and for comparison to established bis(imino)pyridine iron catalysts, we sought to prepare analogous reduced bis(imino)pyridine cobalt dinitrogen compounds. In addition to answering questions relevant to electronic structure, catalytically active cobalt compounds are also of interest because they offer many of the same cost and environmental advantages of iron.

Bis(imino)pyridine cobalt complexes date to Busch's[21] and Sacconi's[22] initial reports of the synthesis and spectroscopic characterization of a variety of halide, nitrate, and thiocyanate derivatives. These classical, Werner-type coordination compounds have received renewed interest following Brookhart's and Gibson's independent discoveries of highly active olefin polymerization catalysts.[4,5] To date, investigations into reduced bis(imino)pyridine cobalt chemistry have been motivated by elucidating the identity of the propagating species during olefin polymerization. Treatment of $(^{iPr}PDI)CoCl_2$ with alkyllithium reagents,[7] Grignard reagents,[23,24] or zinc metal[23] resulted in one-electron reduction to yield the square planar, diamagnetic cobalt monochloride $(^{iPr}PDI)CoCl$. Subsequent alkylation of this species furnished a family of the desired cobalt alkyls $(^{iPr}PDI)CoR$ (R = Me, Et, ^{n}Pr, ^{n}Bu) (Scheme 1).[25,26] Analogous cobalt chloride and alkyl compounds with the phenylated bis(imino)pyridines, $(^{Ar}BPDI)CoCl$ and $(^{Ar}BPDI)CoR$, have also been reported.[27]

Computational studies by Budzelaar and co-workers[28] established that diamagnetic $(^{Ar}PDI)CoCl$, $(^{Ar}PDI)CoR$, and $(^{R'}PDI)CoR$ are best described as low-spin Co(II) complexes ($S_{Co} = 1/2$) antiferromagnetically coupled to a bis(imino)pyridine radical anion ($S_{PDI} = 1/2$). In many cases, low-lying triplet states were found to be only a few kilocalories per mole higher in energy than the ground states. This view of the electronic structure has been corroborated by the observation of bis(imino)pyridine chelate distortions in the solid-state structures as well as the unusual upfield chemical shifts of the in-plane imine methyl groups observed by solution NMR spectroscopy.[7,23,29]

While bis(imino)pyridine cobalt chloride and alkyl compounds with one-electron-reduced chelates have been synthesized and well-studied, formal two- and three-electron reduction products of $(^{Ar}PDI)CoCl_2$ and $(^{iPr}BPDI)CoCl_2$ have not been prepared or characterized. In addition to their potential role in catalysis, these complexes were of interest to determine the degree of chelate participation in the electronic structure and further explore the fundamental concept of redox-active ligands in base metal complexes relevant to catalysis. In addition, these synthetic targets, as in iron chemistry, may also be useful platforms to assemble reactive cobalt−ligand multiple bonds.[30−36] In this paper, we report the results of a combined experimental

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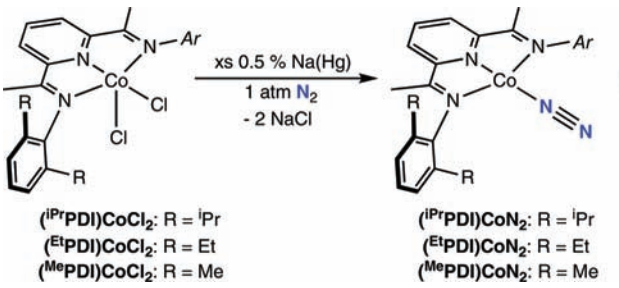
and computational study aimed at evaluating the electronic structure of reduced bis(imino)pyridine cobalt dinitrogen compounds. A homologous series of cationic, neutral, and anionic bis(imino)pyridine cobalt dinitrogen compounds has been studied where the redox states of the compounds differ by three one-electron steps. Electronic structures unique in reduced, base metal bis(imino)pyridine chemistry have been elucidated.

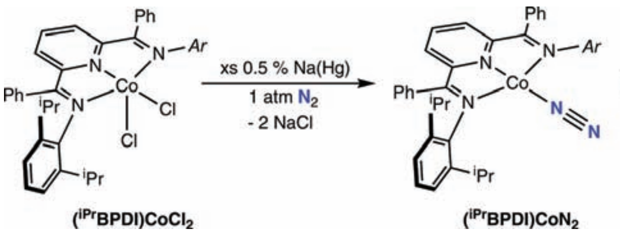
Results and Discussion

Aryl-Substituted Bis(imino)pyridine Cobalt Dinitrogen Complexes. The synthetic methods used to prepare the bis(imino)pyridine iron bis(dinitrogen) complexes (^{iPr}PDI)Fe(N_2)$_2$ and (^{iPr}BPDI)Fe(N_2)$_2$[8] served as the inspiration for study of the analogous cobalt compounds. Stirring toluene solutions of the bis(imino)pyridine cobalt dichloride complexes (^{Ar}PDI)$CoCl_2$ with 6 equiv of sodium amalgam under 1 atm of N_2 for 6 h followed by filtration and recrystallization furnished teal solids identified as the neutral cobalt dinitrogen compounds (^{Ar}PDI)CoN_2 (eq 1). These products were also prepared by addition of 2 equiv of $NaBEt_3H$ to (^{Ar}PDI)$CoCl_2$. Reduction of the diamagnetic bis(imino)pyridine cobalt chloride compounds (^{Ar}PDI)CoCl[7,23] with either 0.5% Na(Hg) or $NaBEt_3H$ also yielded the (^{Ar}PDI)CoN_2 derivatives.



(1)

Two-electron reduction of the phenylated bis(imino)pyridine cobalt dichloride (^{iPr}BPDI)$CoCl_2$ was also attempted. In iron chemistry, (^{iPr}BPDI)Fe(N_2)$_2$ has proven to be a more active catalyst precursor than (^{iPr}PDI)Fe(N_2)$_2$ for 1-hexene hydrogenation, although formation of η^6-arene compounds limited the catalyst lifetime and substrate scope.[8b] The desired cobalt dinitrogen complex (^{iPr}BPDI)CoN_2 was isolated as a dark green solid in 42% yield using an identical procedure used to prepare the (^{Ar}PDI)CoN_2 compounds (eq 2).



(2)

The bis(imino)pyridine cobalt dinitrogen complexes (^{Ar}PDI)CoN_2 and (^{iPr}BPDI)CoN_2 are paramagnetic with solution and solid-state magnetic moments consistent with one unpaired electron and a doublet ground state (see the Experimental Section). One representative example, (^{iPr}PDI)CoN_2, was also studied by variable-temperature SQUID magnetometry (Figure 1). Data were collected on three independently prepared, analytically pure samples, and the individual runs were indistinguishable. (^{iPr}PDI)CoN_2 shows a nearly temperature-independent effective magnetic moment (μ_{eff}) of 1.72 μ_B in the temperature range between 50 and 300 K, which is in excellent agreement with the spin-only value for an $S = 1/2$ ground state (1.73 μ_B). Below 50 K, μ_{eff} declines rapidly to 1.37 μ_B at 5 K due to field saturation effects and weak intermolecular antiferromagnetic coupling that was accounted for by including a small Weiss constant (Θ) of -2 K in the simulation of the data. The isotropic g value of 1.99 that was obtained from the simulation is in good agreement with the g value determined by room temperature EPR spectroscopy (vide infra).

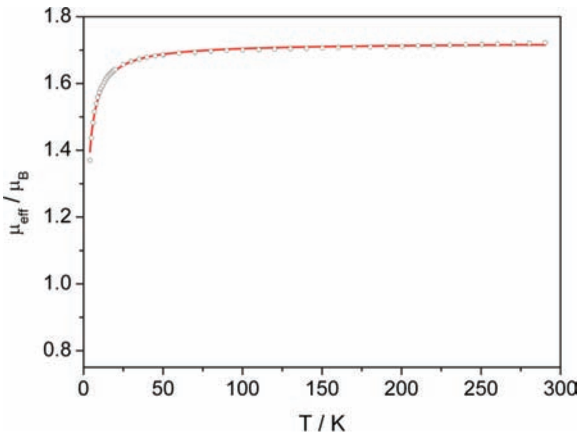


Figure 1. Temperature-dependent SQUID magnetization data (1 T) for samples of (^{iPr}PDI)CoN_2 plotted as a function of the magnetic moment (μ_{eff}) vs temperature (T). The data are corrected for underlying diamagnetism.

The benzene-d_6 ^{1}H NMR spectra of each of the cobalt dinitrogen complexes at 23 °C exhibit three paramagnetically broadened peaks between 2.9 and 6.4 ppm. While observation of only three resonances makes definitive assignment of the individual peaks difficult, the spectra are useful in identifying the presence of the compound and assaying its purity, especially from diamagnetic (^{Ar}PDI)CoCl contaminants. The presence of a dinitrogen ligand was also confirmed by infrared spectroscopy. Toluene solution IR spectra exhibit strong N≡N bands located at 2093 cm^{-1} for (^{iPr}PDI)CoN_2, at 2095 cm^{-1} for (^{Et}PDI)CoN_2, and at 2093 cm^{-1} for (^{Me}PDI)CoN_2. For the phenylated compound (^{iPr}BPDI)CoN_2, this band was observed at 2111 cm^{-1}, consistent with a more electron-withdrawing ligand.[8b] These values are lower than the value of 2184 cm^{-1} reported previously for the cationic bis(imino)pyridine cobalt dinitrogen complex [(^{iPr}PDI)CoN_2][MeB(C_6F_5)$_3$],[23] as is expected for more reduced cobalt compounds.

Because NMR and IR spectroscopies do not determine the amount of N_2 present in bulk samples and identify the presence of possible reduction products that lack dinitrogen, each of the (^{Ar}PDI)CoN_2 complexes was oxidized and the liberated dinitrogen gas quantified with a Toepler pump. Addition of excess $PbCl_2$ to a diethyl ether solution of each of the (^{Ar}PDI)CoN_2 compounds furnished (^{Ar}PDI)$CoCl_2$ and free N_2 gas. In the case of (^{iPr}PDI)CoN_2, 76% of the expected noncombustible gas was collected. For (^{Et}PDI)CoN_2 and (^{Me}PDI)CoN_2, 84% and 83% of the expected dinitrogen gas was obtained, respectively.

Two examples, (^{iPr}PDI)CoN_2 and (^{iPr}BPDI)CoN_2, were characterized by single-crystal X-ray diffraction. A representation of each solid-state structure is presented in Figure 2, and selected bond distances are reported in Table 1. Also included in Table

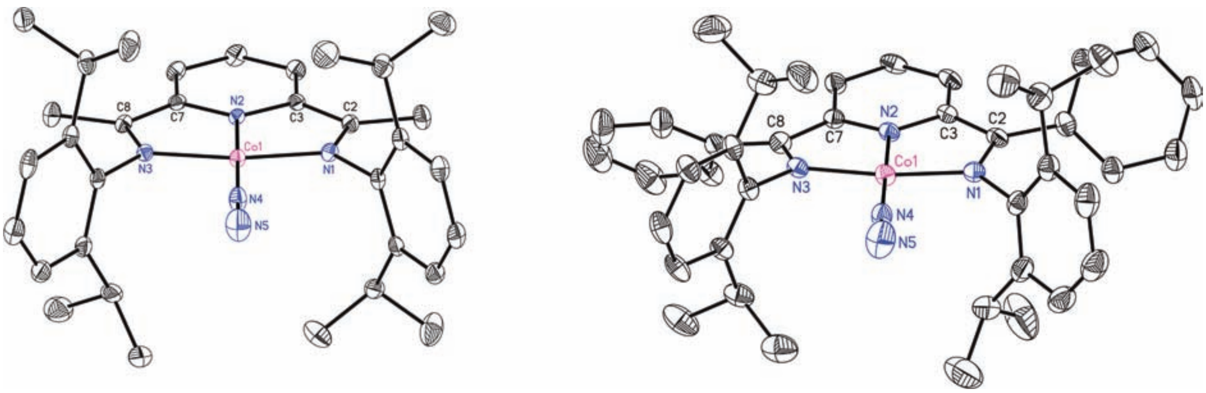


Figure 2. Molecular structures of (^{iPr}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$ at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

1 are the metrical parameters previously reported for (^{iPr}PDI)CoCl$_2$, (^{iPr}PDI)CoCl, and [(^{iPr}PDI)CoN$_2$][MeB(C$_6$F$_5$)$_3$][23] for comparison. For the first two reference compounds, it has been established that the bis(imino)pyridine is in its neutral and monoanionic forms, respectively.[12]

The solid-state structures of (^{iPr}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$ confirm the isolation of four-coordinate, neutral cobalt dinitrogen complexes. The geometry about each cobalt is best described as idealized square planar with the sum of the bond angles equal to 360.01(13)° and 360.03(20)° for (^{iPr}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$, respectively. The N(4)−N(5) distances of the dinitrogen ligands are 1.104(2) and 1.011(3) Å, suggesting little perturbation by the cobalt center. The metrical parameters (Table 1) of the bis(imino)pyridine ligands signal chelate reduction and participation in the electronic structures of the compounds.

In (^{iPr}PDI)CoN$_2$, the C$_{imine}$−C$_{ipso}$ distances are contracted to 1.429(2) and 1.418(2) Å while the C$_{imine}$−N$_{imine}$ bonds are elongated to 1.331(2) and 1.341(2) Å. Slightly less pronounced distortions are present in (^{iPr}BPDI)CoN$_2$, as the C$_{imine}$−C$_{ipso}$ lengths are 1.433(4) and 1.434 Å and the C$_{imine}$−N$_{imine}$ bonds are 1.352(3) and 1.351(3) Å. While the C−C bond distances in (^{iPr}PDI)CoN$_2$ are slightly more contracted than what is usually observed for a monoanionic chelate,[12] the corresponding bond lengths in (^{iPr}BPDI)CoN$_2$ are more typical. Taken on the whole, the ligand perturbations in both compounds are most consistent with a bis(imino)pyridine radical anion. The metal−ligand distances, most notably those associated with the Co−N$_{imine}$ and Co−N$_2$ bonds, in both (^{iPr}PDI)CoN$_2$ and (^{iPr}BPDI)CoN$_2$ are significantly contracted. In the cationic dinitrogen complex [(^{iPr}PDI)CoN$_2$][MeB(C$_6$F$_5$)$_3$], the Co−N distance for the N$_2$ ligand is 1.841(3) Å, while in the neutral compound (^{iPr}PDI)CoN$_2$, the value is 1.7884(16) Å. Contractions of a similar magnitude are observed for the cobalt−imine and −pyridine distances in both neutral dinitrogen compounds.

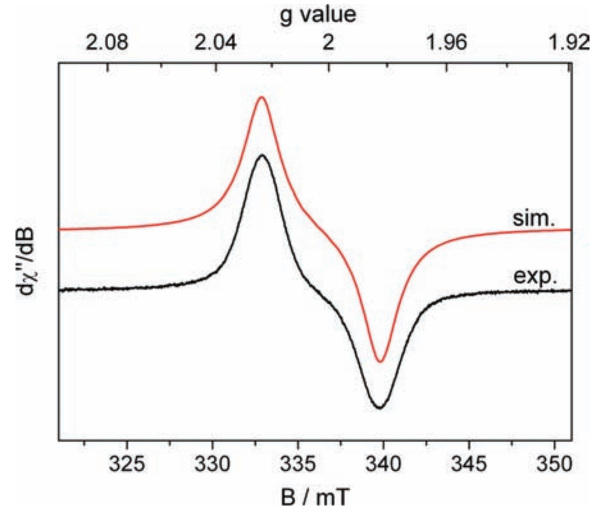


Figure 3. Toluene solution EPR spectrum of (^{iPr}PDI)CoN$_2$ recorded at 23 °C (microwave frequency 9.43 GHz, power 1.26 mW, modulation 1 mT/100 kHz).

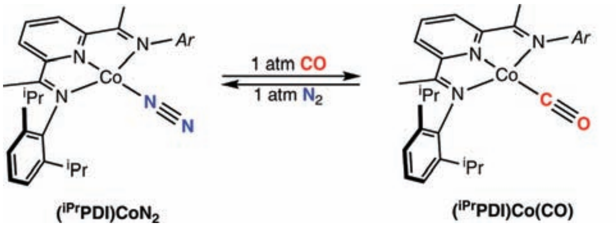
EPR Spectroscopy. The electronic structure of (^{iPr}PDI)CoN$_2$ was also studied by EPR spectroscopy. The X-band EPR spectrum recorded in fluid toluene solution at 23 °C is presented in Figure 3. The spectrum is centered at an isotropic g_{iso} value of 2.003 and shows a distinct separation of the positive and negative derivative peaks, which were assigned to the presence of eight overlapping hyperfine lines, arising from hyperfine coupling of the ligand radical spin to the ^{59}Co nucleus with $I = 7/2$. A corresponding simulation (red line, Figure 3) yields an isotropic hyperfine coupling constant of $A_{iso} = 8 \times 10^{-4}$ cm^{-1} and a line width of 30 × 10^{-4} cm^{-1}. No hyperfine coupling to hydrogen or nitrogen atoms was observed because of the relatively large line width caused by fast relaxation of the cobalt nucleus. The EPR spectrum of a related bis(imino)pyridine compound, (^{iPr}PDI)AlMe$_2$, exhibits a ligand-centered radical with observable hyperfine coupling to ^{15}N and ^{1}H nuclei. The

Table 1. Selected Bond Distances (Å) for (^{iPr}PDI)CoN$_2$, (^{iPr}BPDI)CoN$_2$, (^{iPr}PDI)CoCl$_2$,[6] (^{iPr}PDI)CoCl,[23] and [(^{iPr}PDI)CoN$_2$][MeB(C$_6$F$_5$)$_3$][23]

	(^{iPr}PDI)CoN$_2$	(^{iPr}BPDI)CoN$_2$	(^{iPr}PDI)CoCl$_2$	(^{iPr}PDI)CoCl	[(^{iPr}PDI)CoN$_2$]$^+$
Co−N$_{imine}$	1.8773(14)	1.875(2)	2.211(3)	1.916(3)	1.915(3)
	1.8719(15)	1.872(2)	2.211(3)	1.912(3)	1.908(3)
Co−N$_{pyridine}$	1.8084(14)	1.809(2)	2.051(3)	1.797(3)	1.812(3)
Co−N$_2$	1.7884(16)	1.817(2)			1.841(3)
N$_{imine}$−C$_{imine}$	1.331(2)	1.352(3)	1.280(6)	1.322(5)	1.303(5)
	1.341(2)	1.351(3)	1.285(6)	1.317(5)	1.303(5)
C$_{imine}$−C$_{ipso}$	1.429(2)	1.433(4)	1.483(7)	1.444(5)	1.465(5)
	1.418(2)	1.434(4)	1.481(7)	1.435(5)	1.459(5)
C$_{ipso}$−N$_{pyridine}$	1.379(2)	1.360(3)	1.337(5)	1.373(5)	1.355(4)
		1.366(3)			

magnitude of the hyperfine couplings between the ligand-centered radical and the ^{15}N and ^{1}H nuclei is (1−5) × 10^{-4} cm^{-1} in this case.[37] These couplings are at least 6 times smaller than the line broadening for (^{iPr}PDI)CoN$_2$; therefore, it is unlikely that hyperfine interactions to ^{15}N and ^{1}H would be observed for (^{iPr}PDI)CoN$_2$.

Reactivity of (^{iPr}PDI)CoN$_2$. The synthesis, isolation, and crystallographic characterization of neutral bis(imino)pyridine cobalt dinitrogen complexes prompted exploration of the synthesis of the corresponding isoelectronic carbonyl compounds. Exposure of a toluene solution of (^{iPr}PDI)CoN$_2$ to 1 atm of carbon monoxide at −196 °C followed by warming to 23 °C furnished the red-brown carbonyl complex (^{iPr}PDI)-Co(CO) (eq 3). The benzene-d_6 ^{1}H NMR spectrum recorded at 23 °C exhibits four paramagnetically broadened resonances, similar to the spectrum of (^{Ar}PDI)CoN$_2$. The infrared spectrum of (^{iPr}PDI)Co(CO) in toluene exhibits a single strong C≡O stretch centered at 1975 cm^{-1}, consistent with formation of a monocarbonyl compound. This value is similar to that of one of the bands of the bis(imino)pyridine iron dicarbonyl compound (^{iPr}PDI)Fe(CO)$_2$, which has CO stretching frequencies of 1974 and 1914 cm^{-1}.

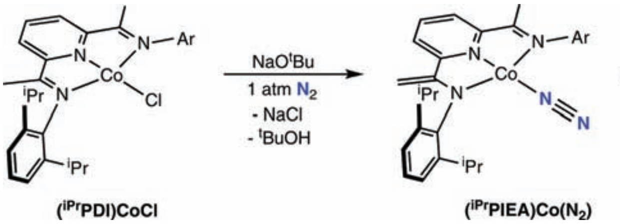


(3)

The relative stabilities of (^{iPr}PDI)CoN$_2$ and (^{iPr}PDI)Co(CO) were probed by in situ infrared spectroscopy. Exposure of a toluene solution of either compound to a vacuum in solution at −78 °C resulted in little to no erosion of either the N$_2$ or CO bands, demonstrating stability to a vacuum at low temperature. However, addition of 1 atm of carbon monoxide to a toluene solution of (^{iPr}PDI)CoN$_2$ at −78 °C cleanly and quantitatively furnished (^{iPr}PDI)Co(CO) with concomitant loss of dinitrogen. Re-exposure of the toluene solution of (^{iPr}PDI)Co(CO) to dinitrogen at −78 °C produced no change, demonstrating the increased binding affinity of carbon monoxide relative to N$_2$.

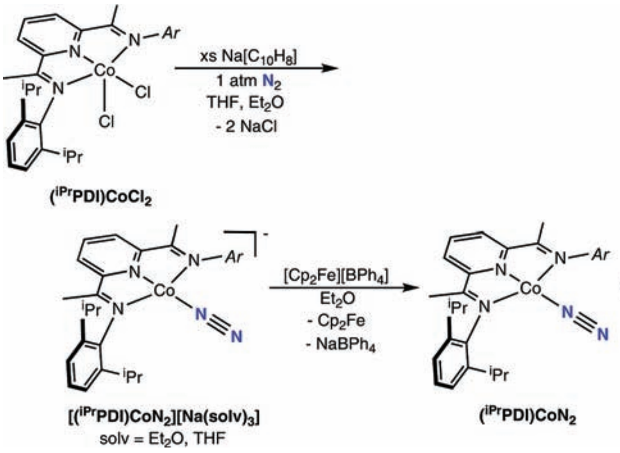
Unlike the iron dicarbonyl complex (^{iPr}PDI)Fe(CO)$_2$, the carbonyl ligand in (^{iPr}PDI)Co(CO) is labile and subject to substitution by dinitrogen at higher temperatures. Allowing a red-brown benzene-d_6 solution of (^{iPr}PDI)Co(CO) to stand at ambient temperature for 6 h in the presence of 1 atm of dinitrogen resulted in a rapid change to green, signaling formation of (^{iPr}PDI)CoN$_2$. Both ^{1}H NMR and IR spectroscopy corroborated formation of the cobalt dinitrogen compound. The conversion of (^{iPr}PDI)Co(CO) to (^{iPr}PDI)CoN$_2$ could be hastened by removing the solvent from the carbonyl compound and preparing solutions of the compound in the presence of N$_2$. CO displacement by N$_2$ was only observed under conditions where dinitrogen was in vast excess.

With a small library of neutral aryl-substituted bis(imino)pyridine cobalt dinitrogen complexes in hand, we sought to prepare other N$_2$ derivatives with different formal cobalt oxidation states for comparison. Previous studies[38−41] have shown that the imine methyl groups of the bis(imino)pyridine chelate are subject to deprotonation and present the opportunity to prepare authentic mono- and dianionic forms of the ligand. Treatment of a THF solution of (^{iPr}PDI)CoCl with 1 equiv of NaO^{t}Bu in the presence of a dinitrogen atmosphere furnished a dark brown powder identified as (^{iPr}PIEA)CoN$_2$, arising from deprotonation of one of the imine methyl groups (eq 4).



(4)

The ^{1}H NMR spectrum of diamagnetic (^{iPr}PIEA)CoN$_2$ exhibits the number of peaks consistent with a C_s-symmetric molecule, signaling imine methyl group deprotonation. Diagnostic olefin peaks are observed at 4.05 and 4.73 ppm in benzene-d_6 for the C=CH_2 positions of the chelate. The intact imine methyl group appears as a singlet at 0.71 ppm. The solid-state (KBr) infrared spectrum also confirmed dinitrogen coordination and imine methyl group deprotonation. A medium-intensity C=C stretch and a strong N≡N band were observed at 1583 and 2148 cm^{-1}, respectively. To compare the N$_2$ stretching frequency of (^{iPr}PIEA)CoN$_2$ to that of (^{iPr}PDI)CoN$_2$, the IR spectrum of the former compound was also recorded in toluene. A strong N≡N stretch was observed at 2145 cm^{-1}, higher in energy than the value of 2093 cm^{-1} recorded for (^{iPr}PDI)CoN$_2$. (^{iPr}PIEA)CoN$_2$ is related to the dimeric variant of the compound prepared by Gambarotta and co-workers, where the monomers are bridged through the intact imine methyl groups.[42] The solid-state infrared spectrum (Nujol) of the dimer exhibits a single strong band at 2153 cm^{-1}, comparable to the value of 2148 cm^{-1} for the monomeric compound described here.



(5)

Because previous studies have shown that the bis(imino)pyridine ligand is capable of accepting up to three electrons,[12a,43] additional reduction chemistry of (^{iPr}PDI)CoN$_2$ was explored. Treating a THF solution of (^{iPr}PDI)CoCl$_2$ with excess (∼3 equiv) sodium naphthalenide for 3 h at 23 °C followed by filtration and recrystallization from diethyl ether furnished a mixture of the cobalt dinitrogen anions, [(^{iPr}PDI)CoN$_2$][Na(solv)$_3$] (solv = THF, Et$_2$O), as judged by solid-state (KBr) infrared spectroscopy (eq 5). For the diethyl ether solvate, a strong N≡N band was observed at 2046 cm^{-1} in toluene solution. The diethyl ether solvate was not isolated free of the THF solvate and was only observed as a mixture by IR spectroscopy following handling of the compound in Et$_2$O. This band shifts substantially to 1981 cm^{-1} for the THF compound. The differences in stretching frequencies are likely a result of the different coordination modes for the sodium atom and its interaction with the N_2 ligand in the cation. In iron chemistry with deprotonated bis(imino)pyridine ligands, Gambarotta and co-workers have observed side-on coordination of a sodium cation with coordinated N_2 in a THF solvate, while end-on sodium coordination with the N_2 ligand was observed in the corresponding ether solvate.[44] Notably, these structural differences are reflected in the N_2 stretching frequencies as the ether solvate has a N≡N band at 1965 cm^{-1}, a value that shifts to 1912 cm^{-1} in the related THF compound. It is likely that a similar effect is responsible for the differences in the cobalt dinitrogen anions described here; however, the lack of structural evidence precludes a definitive rationale. Importantly, in both $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}][\mathrm{Na(solv)_3}]$ compounds, the N_2 stretching frequency is at lower energy than that in the corresponding neutral compound $(^{iPr}\mathrm{PDI})\mathrm{CoN_2}$.

Because of limited solubility, the benzene-d_6 ^1H NMR spectrum of $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}][\mathrm{Na(THF)_3}]$ was recorded in a 1:1 mixture of benzene-d_6 and THF-d_8. Resonances in the typical diamagnetic region were observed. For example, the in-plane imine methyl group appears at 1.85 ppm while the pyridine *meta* and *para* hydrogens appear at 8.39 and 7.07 ppm, suggesting a pure diamagnetic ground state with little to no contribution from triplet excited states.[12b,28] Treatment of a diethyl ether slurry of $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}][\mathrm{Na(THF)_3}]$ with 1 equiv of $[\mathrm{Cp_2Fe}][\mathrm{BPh_4}]$ resulted in quantitative conversion to $(^{iPr}\mathrm{PDI})\mathrm{CoN_2}$ and ferrocene with precipitation of $\mathrm{NaBPh_4}$ (eq 5).

Computational Studies and Evaluation of Electronic Structures. The synthesis of the neutral and anionic cobalt dinitrogen complexes $(^{iPr}\mathrm{PDI})\mathrm{CoN_2}$ and $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}]^-$ in conjunction with the previously reported cationic compound $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}]^+$ provides a rare opportunity to evaluate the electronic structure of a series of molecules that differ by three sequential oxidation states. Holland and co-workers recently reported the synthesis and characterization of both neutral and dianionic, dimeric, β-diketiminate cobalt complexes with bridging end-on dinitrogen ligands and demonstrated the influence of the alkali-metal cations on the weakening of the N≡N bond.[45] In addition to the structural and spectroscopic data described above, DFT calculations using the B3LYP functional were also performed. For the cationic and anionic compounds, only the $[(^{iPr}\mathrm{PDI})\mathrm{CoN_2}]$ portion of the molecule was calculated in the gas phase. No other truncations of the compounds were performed. The optimized geometries for all three of the computed compounds are in reasonable agreement with the available crystallographic data (Table 2). The largest discrepancies are with the Co−N bond lengths, where the B3LYP functional typically overestimates the distances.

Table 2. Comparison of Experimentally Determined and Computed Selected Bond Lengths (Å) of $[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$, $[(^{iPr}\mathrm{PDI}^{\bullet-})\mathrm{Co^IN_2}]$, and $[(^{iPr}\mathrm{PDI}^{2-})\mathrm{Co^IN_2}]^-$

	$[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$		$[(^{iPr}\mathrm{PDI}^{\bullet-})\mathrm{Co^IN_2}]$		$[(^{iPr}\mathrm{PDI}^{2-})\mathrm{Co^IN_2}]^-$
	calcd	exptl[a]	calcd	exptl	calcd
Co(1)−N(1)	1.964	1.908(3)	1.932	1.8719(15)	1.920
Co(1)−N(2)	1.844	1.812(3)	1.839	1.8084(14)	1.830
Co(1)−N(3)	1.965	1.915(4)	1.932	1.8773(14)	1.920
Co(1)−N(4)	1.853	1.841(3)	1.810	1.7884(16)	1.782
N(1)−C(2)	1.302	1.303(5)	1.337	1.341(2)	1.368
N(2)−C(3)	1.347	1.354(4)	1.368	1.379(2)	1.389
N(2)−C(7)	1.347	1.356(5)	1.367	1.367(2)	1.389
N(3)−C(8)	1.302	1.303(5)	1.337	1.331(2)	1.368
C(2)−C(3)	1.479	1.458(5)	1.443	1.418(2)	1.417
C(2)−C(3)	1.479	1.464(4)	1.443	1.429(2)	1.418
N(4)−N(5)	1.102	1.112(5)	1.110	1.104(2)	1.122

[a] From ref 23.

Table 3. Metal Contributions (%) to the Frontier Orbitals of $[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$, $[(^{iPr}\mathrm{PDI}^{\bullet-})\mathrm{Co^IN_2}]$, and $[(^{iPr}\mathrm{PDI}^{2-})\mathrm{Co^IN_2}]^-$

	$[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$	$[(^{iPr}\mathrm{PDI}^{\bullet-})\mathrm{Co^IN_2}]$	$[(^{iPr}\mathrm{PDI}^{2-})\mathrm{Co^IN_2}]^-$
$d_{x^2-y^2}$	73	73	70
PDI a_2	6	12	12
PDI b_2	11	11	10
d_{z^2}	92	88	89
d_{yz}	82	80	75
d_{xz}	79	73	72
d_{xy}	75	77	72

The geometry of the diamagnetic, cationic dinitrogen complex $[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$ was calculated using spin-restricted DFT ($S = 0$). The alternative, spin-unrestricted broken-symmetry (BS) (1,1) solution, corresponding to a $[(^{iPr}\mathrm{PDI}^{\bullet-})\mathrm{Co^{II}N_2}]^+$ formulation, was found to be 8.2 kcal/mol higher in energy. In this solution, the α and β orbitals have different symmetry (metal d_{z^2} (a_1) and ligand b_2). For the spin-restricted solution, the computed C−N and C−C bond distances clearly indicate a neutral, diamagnetic PDI^0 ligand.[12] Accordingly, the a_2 and b_2 orbitals of the bis(imino)pyridine ligand, those typically responsible for redox activity, are empty and constitute the LUMO+1 and LUMO of the complex, respectively. Four doubly occupied metal d orbitals (metal contributions >70% in each case) were found, establishing a low-spin d^8 electronic configuration for the Co(I) center (Table 3). One empty cobalt-based d orbital ($d_{x^2-y^2}$) was also identified. This electronic structure is in agreement with that proposed by Gibson and co-workers[23] and is as expected for a Co(I) complex in a square planar ligand field. Thus, this compound is best described as $[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$.

As established experimentally, the neutral cobalt dinitrogen compound $(^{iPr}\mathrm{PDI})\mathrm{CoN_2}$ has an $S = 1/2$ ground state and was calculated accordingly as a spin-unrestricted doublet. The computed frontier molecular orbital scheme is similar to that for $[(^{iPr}\mathrm{PDI}^0)\mathrm{Co^IN_2}]^+$ with four doubly occupied metal d orbitals and one empty cobalt orbital assigned as $d_{x^2-y^2}$, again establishing a cobalt(I), d^8 center (Table 3). The unpaired electron was located in the b_2 orbital of the bis(imino)pyridine ligand, while the corresponding a_2 orbital remains empty and is the LUMO of the complex. This view of the electronic structure is corroborated by the Mulliken spin density population analysis, which establishes that the unpaired electron is almost exclusively located on the PDI ligand while only a small amount of spin density is transferred to the Co(I) ion by spin polarization (Figure 4).

The computed spin density distribution presented in Figure 4 is in excellent agreement with the experimentally obtained

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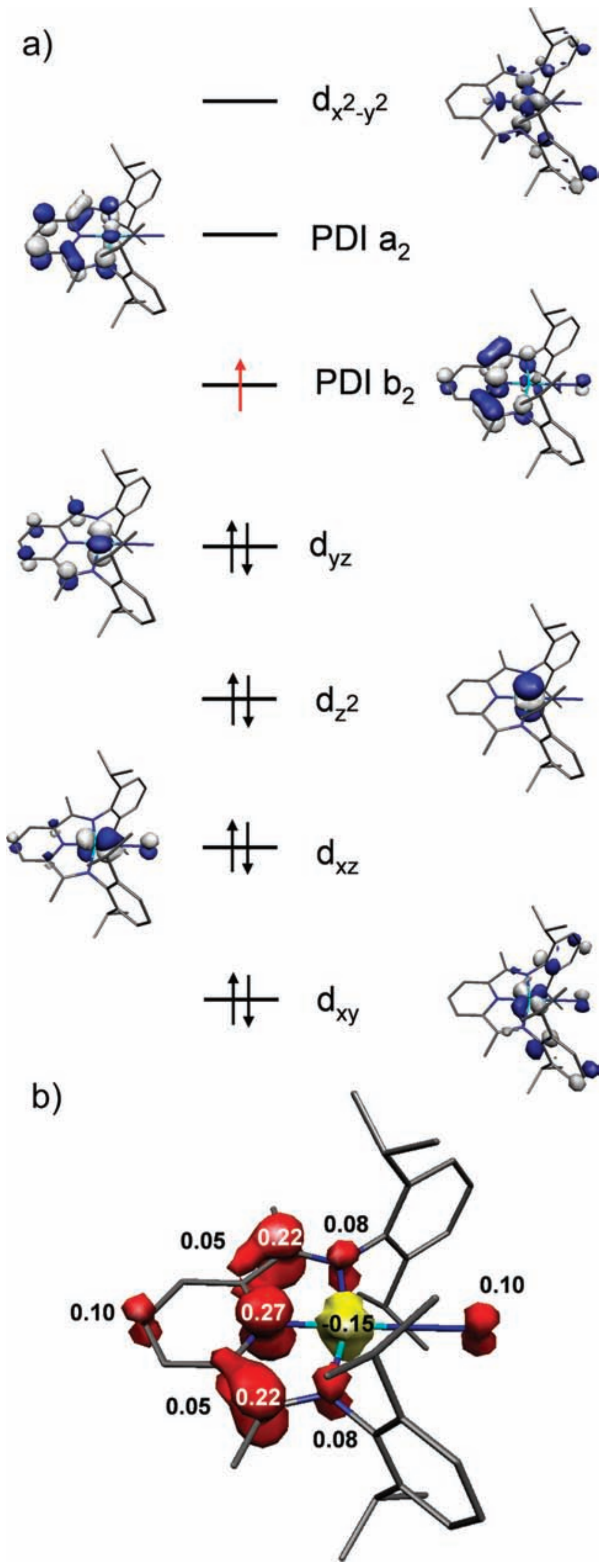

Figure 4. (a) Qualitative molecular orbital diagram for $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ computed from a B3LYP DFT calculation. (b) Spin density plot obtained from a Mulliken population analysis. Positive spin density is shown in red, and negative spin density is shown in yellow. The coordinate system is defined as "z" perpendicular to the idealized square plane of the molecule and "x" along the Co—N≡N vector.

EPR data which exhibit a very small ^{57}Co superhyperfine coupling and almost no g anisotropy, typical for $[PDI]^-$ radicals.[37] The $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ electronic structure description is also consistent with the SQUID magnetization data, which establish a plateau in the effective magnetic moment more consistent with a bis(imino)pyridine radical rather than a cobalt-based SOMO. One discrepancy between the computational and experimental data is the short $C_{imine}-C_{ipso}$ distances of 1.418 and 1.429 Å determined by X-ray diffraction (Table 2). These bond lengths are near the typical range for a dianionic bis(imino)pyridine ligand.[12,12] However, the differences in computational and experimental bond length are not significant within the accepted error of the calculations (0.025 Å), and no such discrepancy was observed between the computational and experimental $C_{imine}-N_{imine}$ distances. A similar overestimation of the $C_{imine}-C_{ipso}$ bond distances was observed for the cationic cobalt dinitrogen complex $[(^{iPr}PDI)CoN_2]^+$. To address this issue, alternative BS(1,2) and BS(3,2) electronic structure descriptions were also calculated to account for potential low- and high-spin Co(II) possibilities, respectively. Both approaches converged to the $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ solution, reaffirming the validity of this description of the compound. Although the $C_{imine}-C_{ipso}$ distances in the solid-state structure of the neutral compound $(^{iPr}PDI)CoN_2$ are more contracted than those of most compounds assigned as having monoreduced chelates,[12] the data for $(^{iPr}BPDI)CoN_2$ are well within the accepted range for a $[PDI^{\bullet-}]$ ligand, and overall the combined spectroscopic and computational data are most consistent with $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$. It should also be noted that both $(^{iPr}PDI)CoCl_2$ and $[(^{iPr}PDI)CoN_2]^+$ are accepted as having neutral bis(imino)pyridine chelates, but the $C_{imine}-C_{ipso}$ and $C_{imine}-N_{imine}$ distances are notably different. Thus, reduction of $[(^{iPr}PDI^{0})Co^{I}N_2]^+$ to $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ is purely ligand-based (Figure 4).

DFT calculations were also performed on the cobalt dinitrogen anion $[(^{iPr}PDI)CoN_2]^-$ using a spin-restricted method. Unfortunately, this compound has eluded structural characterization, and as a result, comparison of computed and experimental metrical parameters was not possible. As with the cationic and neutral cobalt dinitrogen compounds, $[(^{iPr}PDI)CoN_2]^-$ is best described as a cobalt(I) complex with four doubly occupied orbitals and one empty metal-based orbital (Table 3). Thus, one-electron reduction of $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ to $[(^{iPr}PDI^{2-})Co^{I}N_2]^-$ is ligand-based. Consequently, the electronic structure of the anion is very similar to that of the neutral complex with the exception of the now doubly reduced $[PDI]^{2-}$ ligand, which is clearly supported by the computed structural parameters of the ligand (Table 2).[12] Although a high-spin Co(I) configuration is unlikely in an idealized square planar geometry, an open-shell BS(2,2) calculation was performed to exclude the alternative of a triplet ligand coordinated to a high-spin cobalt(I) center. Reassuringly, this computation converged back to the closed-shell singlet solution.

More detailed analysis of the electronic structure of the bis(imino)pyridine dianion reveals coordination of the closed-shell form of the ligand with a doubly occupied b_2 orbital. In related reduced bis(imino)pyridine iron chemistry, previous computational studies have established that the triplet diradical form of the $[PDI]^{2-}$ dianion is favored although the singlet state is only slightly higher in energy and accessible.[12b] The differences in coordination of the singlet versus triplet bis(imino)pyridine dianion can be traced to the d electron configuration of the metal. In the neutral iron dinitrogen complex $(^{iPr}PDI)Fe(N_2)_2$, the metal is in an intermediate-spin d^6 electron configuration ($S_{Fe} = 1$), well poised to antiferromagnetically couple to a chelate triplet diradical dianion. By contrast, the anionic cobalt

Table 4. Comparison of Experimentally Determined and Computed N_2 Stretching Frequencies (cm^{-1})

	$[(^{iPr}PDI^{0})Co^{I}N_2]^+$	$[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$	$[(^{iPr}PDI^{2-})Co^{I}N_2]^-$
exptl	2184	2093	2046
calcd	2190	2114	2041

dinitrogen complex $[(^{iPr}PDI^{2-})Co^{I}N_2]^-$ has a d^8 electronic configuration at cobalt ($S_{Co} = 0$) and is ill-equipped to engage in antiferromagnetic coupling, and hence, the closed-shell form of the dianionic chelate is preferred.

Frequency calculations were also performed at the BP86 level of DFT for all three dinitrogen compounds. Reproducing spectroscopic properties is key to calibrate the computational results against experimental data. The computed and experimental N≡N stretching frequencies are presented in Table 4, and there is excellent agreement with the data. The computations reproduce the N_2 stretching frequencies within 6, 21, and 5 cm^{-1} for the cationic, neutral, and anionic cobalt dinitrogen complexes, respectively, thereby validating the computed models of the electronic structure. For the dinitrogen anion, the diethyl ether solvate was chosen as the experimental comparison likely due to the less perturbing "end-on" coordination of the sodium cation to the terminal N_2 ligand.

The combined experimental and computational data clearly establish the electronic structures for the series of bis(imino)pyridine cobalt dinitrogen complexes (Figure 5). The sequential one-electron reductions from $[(^{iPr}PDI^{0})Co^{I}N_2]^+$ to $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ to $[(^{iPr}PDI^{2-})Co^{I}N_2]^-$ are ligand based. Considering the synthetic sequence used to prepare the neutral dinitrogen compound $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ and the anion $[(^{iPr}PDI^{2-})Co^{I}N_2]^-$ also reveals that one-electron reduction of $[(^{iPr}PDI^{0})Co^{II}Cl_2]$ to $[(^{iPr}PDI^{\bullet-})Co^{II}Cl]$ is ligand based and maintains the Co(II) oxidation state although the metal ion transitions from high spin ($S_{Co} = 3/2$) to low spin ($S_{Co} = 1/2$) due to the increased field strength imparted by the one-electron-reduced bis(imino)pyridine and the square planar geometry. The second one-electron reduction from $[(^{iPr}PDI^{\bullet-})Co^{II}Cl]$ to $[(^{iPr}PDI^{\bullet-})Co^{I}N_2]$ occurs at the metal and preserves the oxidation state of the chelate, likely due to the ligand field stabilization energy derived from a d^8 square planar complex. Once this electronic configuration is achieved, the second bis(imino)pyridine ligand reduction, as evidenced by the synthesis and computation of $[(^{iPr}PDI^{2-})Co^{I}N_2]^-$, is chelate-based due to the relatively high energy of the $d_{x^2-y^2}$ orbital in a square planar ligand field.

Conclusions

Synthesis of neutral and anionic bis(imino)pyridine cobalt dinitrogen complexes has been accomplished, providing the first examples of two- and three-electron reduction products from the corresponding cobalt dichloride compounds. The electronic structure of these compounds, as well as the previously reported cationic dinitrogen compound, was evaluated by spectroscopic and computational methods. Within the series of dinitrogen compounds, bis(imino)pyridine-based reductions were observed with preservation of the Co(I), d^8 configuration. For the neutral compound $(^{iPr}PDI)CoN_2$, the ligand-centered radical was observed by EPR spectroscopy and confirmed by SQUID magnetometry. In the case of the anionic cobalt dinitrogen complex, the bis(imino)pyridine dianion is closed-shell, in contrast to the related iron dinitrogen compound where the triplet diradical is observed. The preference for the closed-shell versus triplet diradical bis(imino)pyridine dianion is determined by the electronic configuration of the metal where intermediate-spin d^6 ferrous anions are well suited for antiferromagnetic coupling to the $S = 1$ diradical while the Co(I), d^8 configuration leaves a low-lying bis(imino)pyridine molecular orbital which favors the singlet state.

Experimental Section[46]

Preparation of $(^{iPr}PDI)Co(N_2)$. A 250 mL round-bottom flask was charged with 21.6 g (107.7 mmol) of Hg, approximately 100 mL of toluene, and a magnetic stir bar. To the flask was added 0.108 g (4.68 mmol) of Na in small pieces with vigorous stirring. The amalgam was stirred for 20 min, and then 0.477 g (0.780 mmol) of $(^{iPr}PDI)CoCl_2$ was added to the flask. A color change to purple over 30 min was initially observed followed by a gradual color change to dark teal. The reaction was stirred for 6 h and then filtered through Celite and concentrated. Cooling the solution to −35 °C afforded 0.301 g (65%) of dark teal crystals identified as (^{iPr}PDI)-

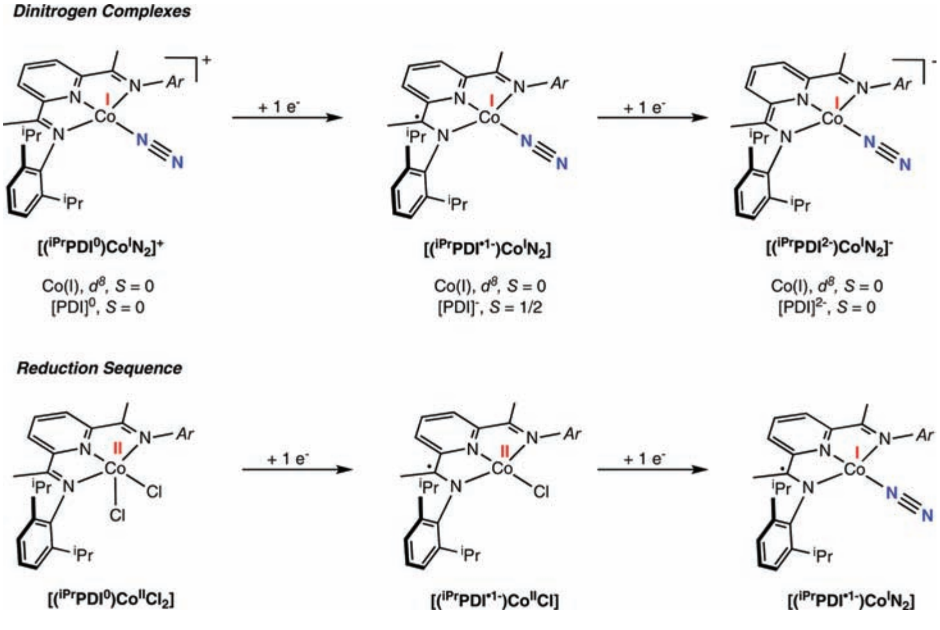

Figure 5. Electronic structure summary for bis(imino)pyridine cobalt dinitrogen complexes and reduction from the corresponding chloride derivatives.

Co(N_2). Anal. Calcd for $C_{33}H_{43}N_5Co$: C, 69.70; H, 7.62; N, 12.32. Found: C, 69.48; H, 7.81; N, 12.07. Magnetic susceptibilty (benzene-d_6, 293 K): $\mu_{eff} = 1.6(2)\ \mu_B$. ^{1}H NMR (benzene-$d_6$): δ = 2.90 (124.5 Hz), 4.27 (242.9 Hz), 6.01 (54.5 Hz). IR (toluene): $\nu_{NN} = 2093\ cm^{-1}$.

Alternative Preparation of (${}^{\text{iPr}}$PDI)Co(N_2). A 250 mL round-bottom flask was charged with 0.502 g (0.821 mmol) of (${}^{\text{iPr}}$PDI)-$CoCl_2$, approximately 100 mL of toluene, and a magnetic stir bar. The reaction was cooled in a liquid nitrogen chilled cold well, and $NaEt_3BH$ (820 μL of a 1.0 M solution, 0.821 mmol) was added dropwise with stirring. The reaction was warmed to room temperature accompanied by a color change to dark purple. The solution was again chilled in the cold well, and $NaEt_3BH$ (820 μL of a 1.0 M solution, 0.821 mmol) was added dropwise. The reaction was warmed to room temperature, resulting in a color change to dark teal. The solution was filtered through Celite, concentrated, and cooled to −35 °C and yielded 0.294 (63%) of dark teal crystals of (${}^{\text{iPr}}$PDI)Co(N_2).

Preparation of (${}^{\text{iPr}}$BPDI)Co(N_2). A 100 mL round-bottom flask was charged with 16.6 g (82.8 mmol) of Hg, approximately 50 mL of toluene, and a magnetic stir bar. To the flask was added 0.083 g (3.61 mmol) of Na in small pieces with vigorous stirring. The amalgam was stirred for 20 min, and then 0.467 g (0.635 mmol) of (${}^{\text{iPr}}$BPDI)$CoCl_2$ was added to the flask. A color change to dark red over 30 min was initially observed followed by a gradual color change to forest green. The reaction was stirred for 24 h and then filtered through Celite and concentrated. Cooling the solution to −35 °C afforded 0.185 g (42%) of forest green crystals identified as (${}^{\text{iPr}}$BPDI)Co(N_2). Anal. Calcd for $C_{43}H_{47}N_5Co$: C, 74.55; H, 6.85; N, 10.11. Found: C, 74.71; H, 6.73; N, 9.91. Magnetic susceptibilty (benzene-d_6, 293 K): $\mu_{eff} = 1.1(3)\ \mu_B$. ^{1}H NMR (benzene-$d_6$): δ = 3.61 (at least 350 Hz), 3.78 (at least 350 Hz), 5.58 (192.65 Hz). IR (toluene): $\nu_{NN} = 2111\ cm^{-1}$.

Preparation of [(${}^{\text{iPr}}$PDI)Co(N_2)][Na(solv)$_3$]. Sodium naphthalenide was prepared in situ by addition of approximately 50 mL of tetrahydrofuran to a 100 mL round-bottom flask containing 0.026 g (1.13 mmol) of sodium metal and 0.147 g (1.14 mmol) of naphthalene. The reaction was stirred for 3 h, during which time the solution became green in color and homogeneous. After this time, 0.200 g (0.327 mmol) of (${}^{\text{iPr}}$PDI)$CoCl_2$ was added to the flask, and the reaction was stirred for 1 h, after which time the volatiles were removed. The residual solid was extracted into diethyl ether and stirred for 1 h, producing a bright green solution. The solution was filtered through Celite, concentrated, and cooled to −35 °C to yield forest green crystals identified as a mixture of [(${}^{\text{iPr}}$PDI)Co-(N_2)][Na(Et_2O)$_3$] and [(${}^{\text{iPr}}$PDI)Co(N_2)][Na(THF)$_3$]. Dissolution of the crystals in tetrahydrofuran followed by removal of volatiles resulted in quantitative conversion to [(${}^{\text{iPr}}$PDI)Co(N_2)][Na(THF)$_3$] (0.277 g, 52%). Anal. Calcd. for $C_{45}H_{67}N_5O_3NaCo$: C, 66.89; H, 8.36; N, 8.67. Found: C, 66.91; H, 8.60; N, 8.69. ^{1}H NMR (1:1 THF-d_8/benzene-d_6): δ = 1.19 (s, 24H, CH(C*H*$_3$)$_2$), 1.85 (s, 6H, C(C*H*$_3$)), 3.02 (s, 4H, C*H*(CH$_3$)$_2$), 7.07 (s, 1H, pyridine *para*), 7.25 (s, 4H, aryl *meta*), 7.36 (s, 2H, aryl *para*), 8.39 (s, 2H, pyridine *meta*). IR (KBr): $\nu_{NN} = 2046\ cm^{-1}$ (solv = Et_2O), 1981 cm^{-1} (solv = THF).

Spectroscopic Characterization of (${}^{\text{iPr}}$PDI)Co(CO). A J. Young NMR tube was charged with 0.009 g (0.016 mmol) of (${}^{\text{iPr}}$PDI)-Co(N_2) in benzene-d_6. The tube was degassed, and 20 equiv (50 Torr in a 100.1 mL gas bulb) of carbon monoxide was added at −196 °C. Upon warming to room temperature, there was a rapid color change to red-brown. ^{1}H NMR spectroscopy confirmed quantitative conversion to (${}^{\text{iPr}}$PDI)Co(CO). The infrared spectrum of (${}^{\text{iPr}}$PDI)Co(CO) was obtained by exposing a 7.0 mM solution of the compound to an atmosphere of carbon monoxide in a three-neck flask containing the infrared probe. ^{1}H NMR (benzene-d_6): δ = 2.63 (183.6 Hz), 3.21 (140.3 Hz), 6.03 (256.7 Hz), 10.62 (405.5 Hz). IR (toluene): $\nu_{CO} = 1975\ cm^{-1}$.

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Supporting Information Available: Additional experimental procedures and crystallographic details for (${}^{\text{iPr}}$PDI)CoN_2 and (${}^{\text{iPr}}$BPDI)CoN_2 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Representative experimental procedures are reported here. General considerations, computational details, and additional experimental procedures and spectroscopic data are reported in the Supporting Information.