Dinitrogen activation by a low-valent cobalt complex and the elusive cobalt-oxo.

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Introduction:

1.1 Background

Dinitrogen is an inert triply bonded diatomic molecule. It is very difficult to activate because of its high ionization potential (15.058 eV), negative electron affinity (-1.8 eV) and high bond dissociation energy (945 kJ/mol).[1] The lack of reactivity of N_2 is not simply due to the triple bond; carbon monoxide is isoelectronic with dinitrogen but undergoes a variety of chemical reactions but yet has a greater bond dissociation energy (1076 kJ/mol).[2] This variation suggests that something else is responsible for the inertness of dinitrogen, besides polarity. When looking at the molecular orbital diagram of N_2, it contains a low energy HOMO (–15.6 eV) and a high energy LUMO (7.3 eV), thus creating a large HOMO/LUMO energy gap which disfavors electron transfer and Lewis acid/base chemistry.[3]

One major challenge still facing chemists today is the utilization of molecular nitrogen or dinitrogen in the generation of nitrogen containing products of synthetic utility.[1] Development of synthetic alternatives for the activation of dinitrogen by transition metals has been the main goal of research over the past 40 years, especially for the understanding of biological dinitrogen fixation. Nature converts N_2 from the atmosphere into a form readily utilizable by organisms using a class of enzymes called nitrogenases.[4] The most well characterized and studied nitrogenase enzyme contains the Mo-Fe cofactor at its active site which is able to bind dinitrogen and convert it to ammonia catalytically and under normal conditions. Despite the efforts of many scientists, the exact mechanism by which

this Mo-Fe cofactor works is still unknown.[4] Crystallographic data has more recently shown that the cofactor has a cage-like arrangement of one molybdenum and seven iron centers linked by sulfide ions with an additional atom, possibly N, C, or O occupying the central cavity (Figure 1.1).[5] Re-evaluation of the current theories is necessary in understanding the interaction of the nitrogenase enzyme with dinitrogen and the role of molybdenum-iron cofactor.[6] Chatt et al. utilized low oxidation state Group 6 metal centers supported by ancillary phosphane ligands to create monometallic dinitrogen complexes.[7] These systems reacted with reducing agents and protons to generate reduced nitrogen containing complexes, including hydrazine and ammonia.[7]
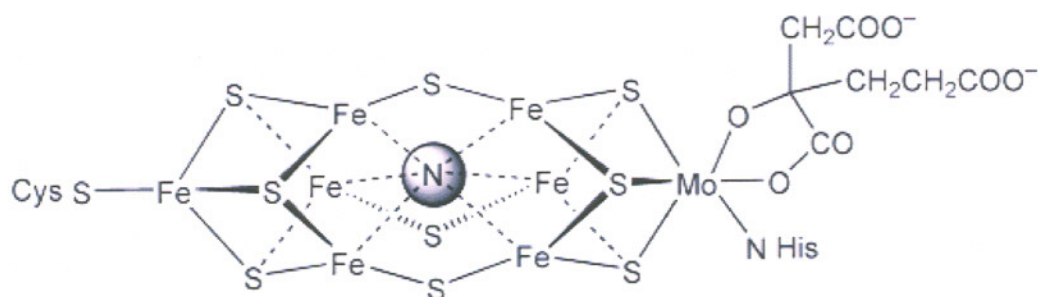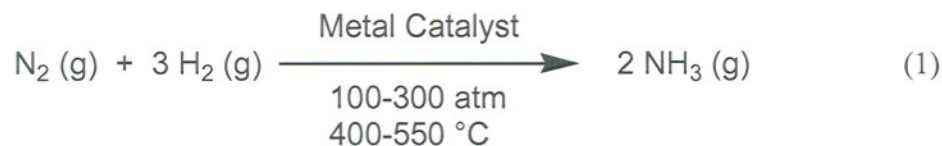

Figure 1.1 Structure of Mo-Fe nitrogenase enzyme.

Chemists are not only looking into the enzymatic use of dinitrogen, they are also currently investigating ways to utilize nitrogen gas to synthesize various complex molecules, containing nitrogen and to understand the mechanistic process of converting N_2^0 to $2 N^{3-}$. The Haber-Bosch process is the only commercially successful method that utilizes nitrogen gas. This process involves the reaction of N_2 with three equivalents of H_2 over a ruthenium or iron based

catalyst to produce ammonia (Eq. 1).[1] Haber won the 1918 Nobel Prize in

chemistry for providing a route that utilized fixed nitrogen in the form of

ammonia, widely used as

$$N_2 \text{ (g)} + 3 H_2 \text{ (g)} \xrightarrow[\substack{100\text{-}300 \text{ atm} \\ 400\text{-}550 \text{ °C}}]{\text{Metal Catalyst}} 2 NH_3 \text{ (g)} \tag{1}$$

fertilizer.[1] In 1931, Bosch was awarded the Nobel Prize (shared with Berpius)

because of his development of the high-pressure techniques that made the

synthesis of ammonia feasible industrially.[1]

1.2   Coordination Chemistry of Dinitrogen

Currently the focus of the scientific literature is on the synthesis of a

complex that is able to coordinate dinitrogen and then undergo addition of

electrons/protons/ or other reducing agents.[1] More specifically, N_2 group transfer

to organic moieties is a significant goal. Numerous N_2 complexes are known,

however only a few have shown the ability to reduce N_2 to NH_3

stoichiometrically.[8] In 1965, Allen and Senoff isolated $[Ru(NH_3)_5(N_2)]^{2+}$ and

discovered that $[Ru(NH_3)_5]^{2+}$ could reversibly coordinate dinitrogen.[9] This result

sparked the interest in the coordination chemistry of dinitrogen.[9] While other

systems have shown to coordinate dinitrogen, transition metals and more recently

lanthanides have dominated the coordination chemistry of dinitrogen.

In order to rationalize the activation of a dinitrogen ligand in a transition

metal complex, the Dewar-Chatt-Duncanson synergistic bonding model must be

analyzed. There are three different coordination modes for dinitrogen: end-on

$(A)^9$, end-on bridging (B),[10] and side-on (C)[11] (Figure 1.2). If the dinitrogen is

bound end-on to a single metal center, the filled N_2 nonbonding σ orbital forms a

A N-N = 1.14 Å

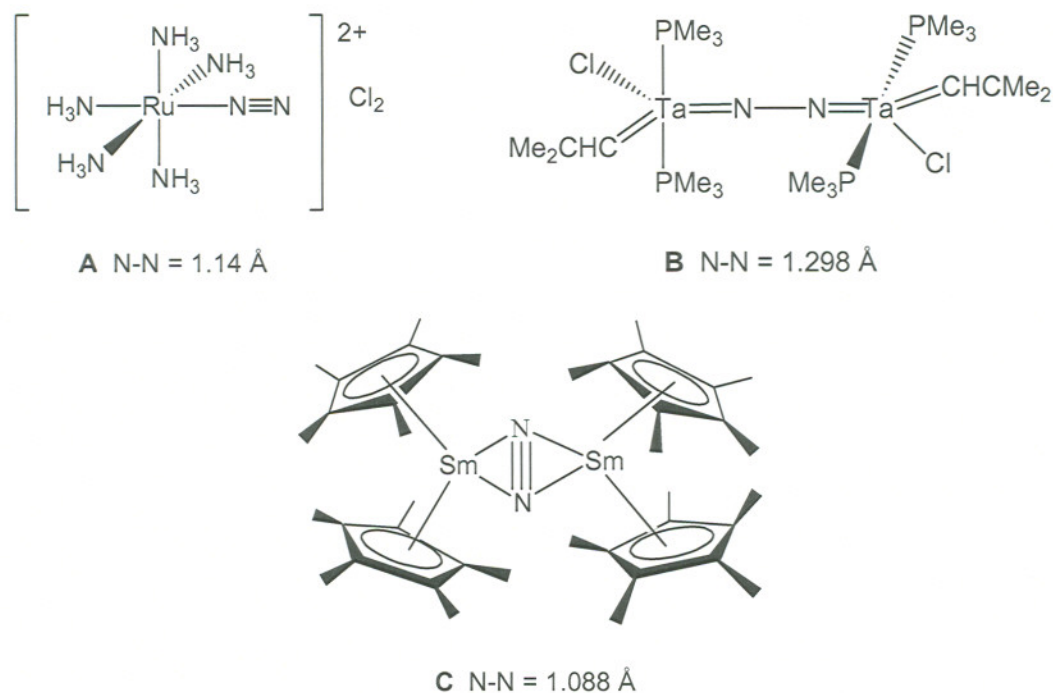**B** N-N = 1.298 Å

C N-N = 1.088 Å

Figure 1.2 Three complexes exhibiting the different coordination modes of N_2.

dative bond with the metals empty dz^2 or $dx^2\text{-}y^2$ orbitals.[1] The π component is the

result of the back bonding of the filled dxz, dyz or dxy orbitals into the vacant π^*

orbital of N_2, stabilizing the metal-N_2 complex. The same applies for the side-on

coordination mode, except the ligand donor orbital is the π_u and only one π_g^*

orbital has the symmetry to be a π-acceptor.[1] Since the stability of the N_2 lone

pair and the large HOMO/LUMO gap minimizes the metal and N_2 overlap,

dinitrogen is considered to be both a poor σ donor and poor π acceptor.[1]

Activation can be achieved when dinitrogen bridges two metal centers.

The basicity is increased with back-donation; the donation from one metal renders

it a better base to the second metal.[1] Example B in Figure 1.1 demonstrates a

more reduced form of the metal to nitrogen bond, with a partially reduced example containing an alternating single-double bond motif (M-N=N-M) and a completely reduced form would contain a metal nitrogen triple bond as seen by Cummins in his $N \equiv Mo[N(Bu^t)Ph]_3$.[11b]

Donation of electrons into N_2 causes the bond order to be reduced; formalism for the reduction to N=N double bond $(N_2)^{2-}$ or an N-N single bond $(N_2)^{4-}$ has been used to describe many systems.[1] The N-N bond lengths determined by crystallographic data are also used to determine bond order; a N_2 triple bond is 1.097 Å, N=N is 1.23 Å, and a single bond is 1.454 Å. Infrared or Raman stretching frequency ν(N-N) is indicative of bond order or degree of activation, the lower the frequency, the longer the N-N bond.[1] These experimental observations along with the formal oxidation state of the metal center must be examined to determine the bond order.

1.3   Research Objectives:

Investigation of an anionic pincer type ligand, PNP (PNP = $N[2-P(CHMe_2)_2-4-Me-C_6H_3]_2^-$) (Figure 1.3), which combines a hard amine and two soft phosphine donors to a transition metal, is currently underway. Additionally, there is precedence for dinitrogen activation by cobalt complexes, exploration of the reactivity of [PNP]− with cobalt is also being explored.

Another avenue of analysis is the chemistry of cobalt imido complexes of the type [PNPCo=NR], an investigation that stems from their isoelectronic relationship to the elusive [PNPCo=O]. The oxo species has evaded direct

observation, and to our knowledge no terminal oxo cobalt complex has ever been

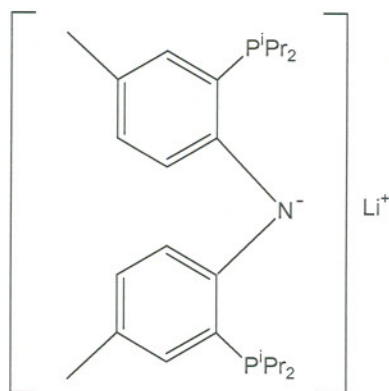isolated. The synthesis and characterization of the first cobalt dinitrogen

Figure 1.3. The [PNP]⁻ ligand.

compound containing the PNP ligand as well as the synthesis of cobalt imido and

oxo complexes will specifically be carried out.

Results and Discussion

2.1 Synthesis of Li(PNP)

The ligand Li(PNP) (PNP$^-$ = N(2-P(^{i}Pr$_2$)$_2$,4-Me-phenyl)$_2$) a pincer-type ligand recently described by Ozerov,[12] was isolated (Scheme 2.1) and closely
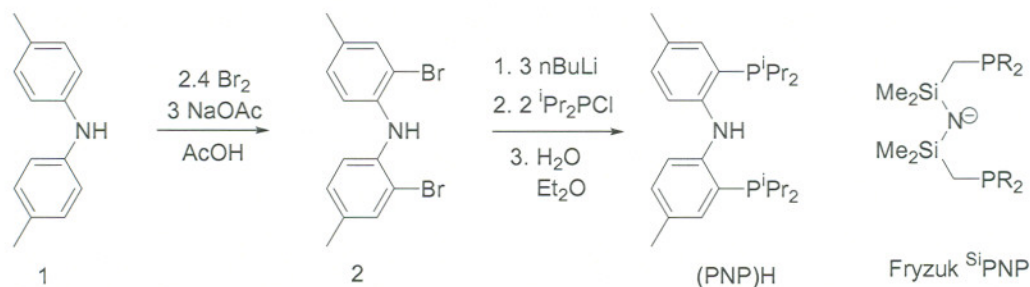

Scheme 2.1 Synthesis of (PNP)H and the similar PNP ligand utilized by Fryzuk.

resembles the ligand utilized by Fryzuk.[13] One major difference between the two

is more robust N-C bonds have replaced the labile N-Si bonds of Fryzuk's ligand.

An advantage of the latter is that it is more flexible and hence not restricted to

constrained geometries, while the PNP$^-$ ligand is rigidly fixed and prefers

meridional coordination to a metal center. The tridentate PNP$^-$ ligand imposes a

unique electronic environment with a hard amide donor and two soft phosphine

donors. Preparation of 1 (Scheme 2.1) and its bromination product 2, undergoes a

one-pot deprotonation and lithium-bromine exchange to generate the trilithio

derivative of 2. This was then phosphinated with ^{i}Pr$_2$PCl to provide (PNP)H upon

hydrolysis.[12] ^{n}BuLi was added to give the lithiated product of (PNP)H, a yellow

solid in ca.65 % yield.

2.2 Synthesis of (PNP)CoCl (1)

The (PNP)CoCl complex was obtained by reacting CoCl$_2$ with Li(PNP) in

THF at -35 °C and was isolated as a dark blue solid in 76 % yield (Scheme 2.2).

The paramagnetic Co (II) compound is soluble in Et_2O, toluene, benzene and THF. The room temperature toluene solution magnetic moment was determined by the method of Evans and provided a value of 2.32 μ_B which implies a low spin Co(II) ion confined in a square planar geometry. Magnetic moments for Co(II)
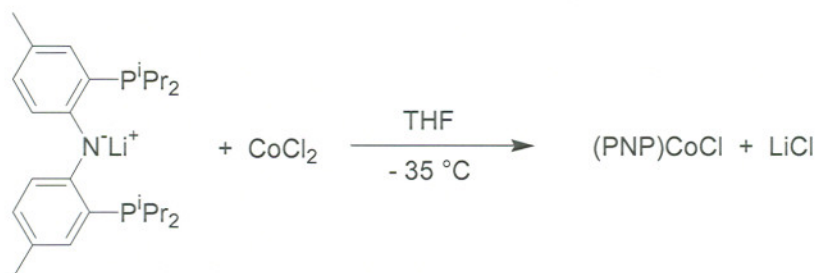
Scheme 2.2 Synthesis of (PNP)CoCl.

tetrahedral and pseudotetrahedral structures typically fall within a range of 4.3 and 5.2 μ_B and are assigned high spin.[13b]

Single crystals of (PNP)CoCl (1) suitable for X-ray diffraction study were obtained by cooling a saturated toluene solution of the complex (Figure 2.1). Selected bond lengths and angles are presented in Table 2.1 and the cobalt chloride complex displays a square planar geometry around the cobalt center.
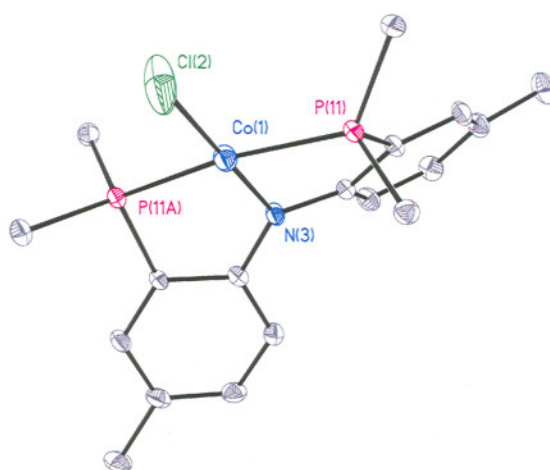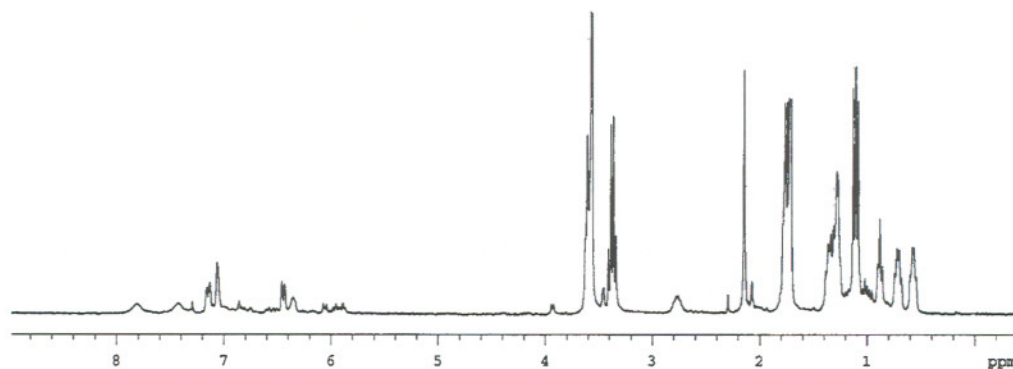

Figure 2.1 Molecular structure of 1 with thermal ellipsoids at the 50% probability level. (^{i}Pr's and H's have been omitted for clarity).

Table 2.1 Selected bond lengths (Å) and angles (°) for (PNP)CoCl.

Co-N(3)	1.905(3)	N(3)-Co-Cl(2)	180.000(1)
Co-Cl(2)	2.1919(14)	N(3)-Co-P(11)	83.82(2)
Co-P(11)	2.2203(7)	Cl(2)-Co-P(11)	96.18(2)
Co-P(11)#1	2.2203(7)	N(3)-Co-P(11)#1	83.82(2)
		Cl(2)-Co-P(11)#1	96.18(2)
		P(11)-Co-P(11)#1	167.63(4)

2.4 Synthesis of $[Na_2(thf)_3][(PNP)Co(N_2)]$ (2)

Dropwise addition of (PNP)CoCl (1) in THF to a rigorously stirred

solution of sodium napthalenide resulted in the formation of the dianionic

dinitrogen cobalt complex (2) in 62 % yield (Scheme 2.3). Formation of complex

2 was confirmed by [1]H (Figure 2.2) and ^{31}P NMR spectra consistent with a

$$(PNP)CoCl \; + \; 30 \; Na \; + \; \text{(naphthalene)} \; \xrightarrow{\text{THF}} \; [Na_2(thf)_3][(PNP)Co(N_2)]$$

Scheme 2.3 Synthesis of $[Na_2(thf)_3][(PNP)Co(N_2)]$.

Figure 2.2 ^{1}H NMR spectra of $[Na_2(thf)_3][(PNP)Co(N_2)]$.

diamagnetic cobalt(-1) complex. The ^{31}P NMR displays a broad single peak at

65.8 ppm.

    To ascertain the formation of a N_2 complex and the degree of reduction of

the N_2, we collected single crystals suitable for x-ray diffraction of complex 2

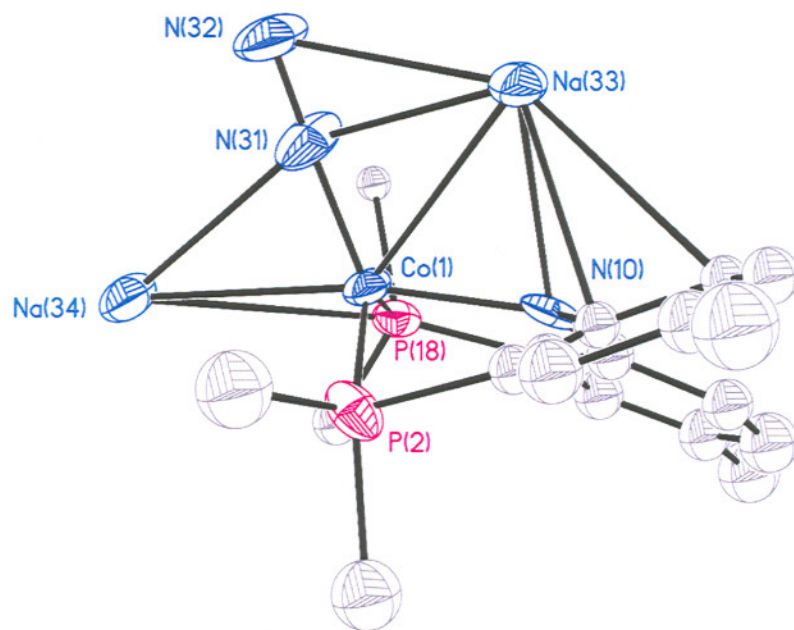(Figure 2.3), selected bond lengths and angles are provided in Table 2.2. The

Figure 2.3 Molecular structure of 2 with thermal ellipsoids at the 50%
              probability level. (^{i}Pr's, thf and H's have been omitted for clarity).

Table 2.2 Selected bond lengths (Å) and angles (°) for $[Na_2(thf)_3][(PNP)Co(N_2)]$

Co-N(31)	1.717(7)	N(31)-Co-N(10)	117.9(3)
Co-N(10)	2.051(7)	N(31)-Co-P(2)	114.3(3)
Co-P(2)	2.138(3)	N(10)-Co-P(2)	83.2(2)
Co-P(18)	2.149(3)	N(31)-Co-P(18)	110.6(3)
Co-Na(34)	2.726(4)	N(10)-Co-P(18)	86.6(2)
Co-Na(33)	2.863(3)	P(2)-Co-P(18)	133.44(9)
N(31)-N(32)	1.181(8)	N(31)-Co-Na(34)	72.6(3)
		N(31)-Co-Na(33)	58.4(3)
		P(2)-Co-Na(34)	93.77(13)
		P(2)-Co-Na(33)	101.05(11)

crystal structure of $[Na_2(thf)_3][(PNP)Co(N_2)]$ is strong evidence for the first

monomeric dianionic dinitrogen complex. In 2 there are four possible oxidation

states for the cobalt metal center either Co(I), Co(II), Co(III), or Co(-I),

comparison to the literature,[14-15,18,21] collected NMR data, and crystal data

suggests a Co(-1) metal center (Figure 2.4). The Co-N bond length of 1.731 Å is

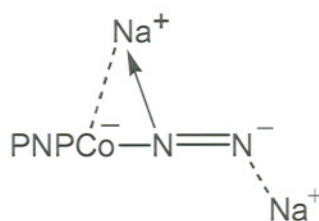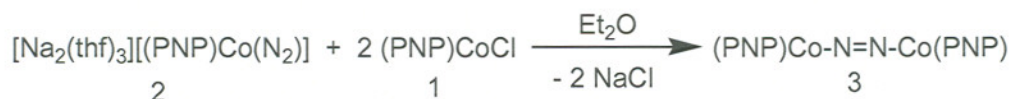indicative of a single bond while the N-N distance of 1.181 Å is indicative of a

double bond.

$$Na^+$$

$$PNP\overset{-}{Co}—N\!\!=\!\!N^-$$

$$Na^+$$

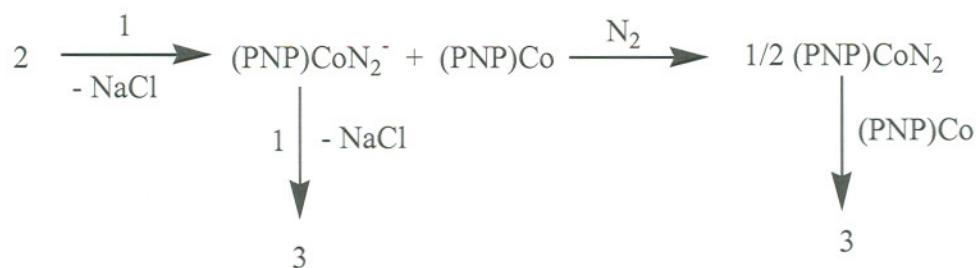**Figure 2.4** Explanation of negative charge on the cobalt metal center.

2.5 Synthesis of (PNP)Co-N=N-Co(PNP) (3)

Complex 3 was readily obtained from the reaction of 2 and two

equivalents of 1 in diethyl ether (Scheme 2.4). In order to balance the equation

$$[Na_2(thf)_3][(PNP)Co(N_2)] \ + \ 2\,(PNP)CoCl \ \xrightarrow[-\ 2\ NaCl]{Et_2O} \ (PNP)Co\text{-}N\text{=}N\text{-}Co(PNP)$$

$$\qquad\qquad 2 \qquad\qquad\qquad\qquad 1 \qquad\qquad\qquad\qquad\qquad\qquad 3$$

Scheme 2.4 Synthesis of (PNP)Co-N=N-Co(PNP).

another (PNP)Co must undergo N_2 binding, the mechanism can best be explained

by Scheme 2.5. Complex 3 was isolated as a black solid and is soluble in polar

solvents and also in aliphatic hydrocarbons. The ^{31}P NMR shows two broad

peaks at 50.3 and 58.0 ppm and the ^{1}H NMR is indicative of a diamagnetic Co(I)

complex.

$$2 \xrightarrow[\text{- NaCl}]{1} (PNP)CoN_2^- + (PNP)Co \xrightarrow{N_2} 1/2 \ (PNP)CoN_2$$

$$1 \downarrow \text{- NaCl} \qquad\qquad \downarrow (PNP)Co$$

$$3 \qquad\qquad\qquad 3$$

Scheme 2.5 Mechanism for the synthesis of (3).

Single crystals of (PNP)Co-N=N-Co(PNP) suitable for X-ray diffraction study were obtained by slow evaporation of a diethyl ether solution of the complex. Both cobalt metal centers of the dimer are in a square planar geometry bridged by N_2, illustrated in the molecular structure (Figure 2.5). Selected bond lengths and angles are presented in Table 2.3. The dimer contains no crystallographic inversion center at the N(4)-N(3) bond indicative of the reduced symmetry noted in the crystal structure. Comparison of both dinitrogen compounds (2 and 3) to an array of known cobalt dinitrogen complexes of varying oxidation state (Table 2.4) display similar geometry and bond lengths/angles.
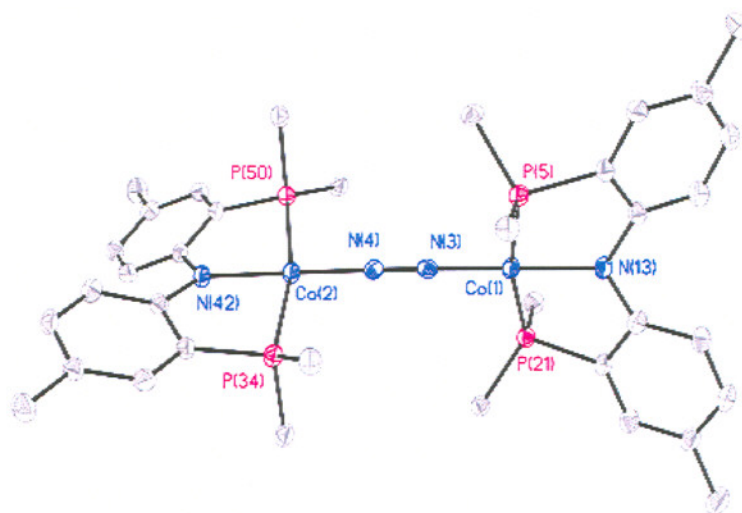

Figure 2.5 Molecular structure of 3 with thermal ellipsoids at the 50% probability level. (^{i}Pr's and H's have been omitted for clarity).

Table 2.3 Selected bond lengths (Å) and angles (°) for 3.

Co(1)-N(3)	1.763(2)	N(3)-Co(1)-N(13)	179.66(8)
Co(1)-N(13)	1.928(2)	N(3)-Co(1)-P(21)	96.42(6)
Co(1)-P(21)	2.2033(7)	N(13)-Co(1)-P(21)	83.25(6)
Co(1)-P(5)	2.2043(7)	N(3)-Co(1)-P(5)	96.70(6)
Co(2)-N(4)	1.768(2)	N(13)-Co(1)-P(5)	83.62(6)
Co(2)-N(42)	1.935(2)	P(21)-Co(1)-P(5)	166.81(3)
Co(2)-P(34)	2.1895(7)	N(4)-Co(2)-N(42)	179.00(8)
Co(2)-P(50)	2.1981(7)	N(4)-Co(2)-P(34)	95.30(6)
N(3)-N(4)	1.144(3)	N(42)-Co(2)-P(34)	83.85(6)
		N(4)-Co(2)-P(50)	96.88(6)
		N(42)-Co(2)-P(50)	83.96(6)
		P(34)-Co(2)-P(50)	167.75(3)

Table 2.4 List of bond lengths of cobalt dinitrogen complexes.

Complex	Ox. State	Co-N (Å)	N-N (Å)	Ref.
$[Na_2(thf)_3][(PNP)Co(N_2)]$	I	1.717(7)	1.181(8)	
$(PNP)Co-N=N-Co(PNP)$	I	1.763(2)	1.144(3)	
$\{((CH_3)_3P)_3CoN_2\}_2\,Mg(THF_4)$	-I	1.72	1.18	14
$K[N_2Co(P(Me)_3)_3]$	-I	1.70(2)	1.17(3)	15
$[(Me_3P)_3CoN_2MgCMe_3(OEt_2)]_2$	-I	1.211(4)	1.672(3)	15
$[(Me_3P)_3CoN_2AlMe_2]_2$	-I	1.252(6)	1.642(4)	15
$2,6-[CMe=N(2,6-C_6H_3Pr^i_2)]_2$ $C_5H_3N]CoN_2$	I	1.841(3)	1.112(6)	16
$\{[(tppme)Co]_2(\mu-N_2)$	0	1.76(1)	1.18(2)	17
$[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$	-I	1.707(11)	1.167(16)	18
$[Co(N_2)(PPh_3)_3]Li(THF)_3$	-I	1.624(26)	1.19(4)	18
$[(Tp^{Np}Co)_2(\mu-N_2)]$	I	1.774(22), 1.847(21)	1.141(30)	19
$[Co(\mu-t-Bu_2P)N_2(PMe_3)]_2$	I	1.814(4)	1.092(5)	20
$[(Me_3P)_3CoN_2AlMe_2]_2$	-I	1.642(4)	1.252(6)	21

2.6 Synthesis of (PNP)Co(OCPh₃) (4)

The compound (PNP)Co(OCPh₃) (4) was readily prepared by reacting

equimolar amounts of (1) and NaOCPh₃ in THF, a dark blue solid was isolated in

ca. 80% yield after the appropriate workup (Scheme 2.5). The ¹H NMR indicates

$$(PNP)CoCl + NaOCPh_3 \xrightarrow{THF} (PNP)Co(OCPh_3)$$

Scheme 2.5 Synthesis of PNPCoOCPh$_3$.

that the cobalt (II) complex is paramagnetic which is also apparent by the silence

of the ^{31}P NMR spectra. Complex 4 was synthesized with the aim of obtaining

the first cobalt oxo (Co=O) complex. The formation of the cobalt-oxo is

dependent upon the ejection of the stable radical CPh$_3$, a scenario that is highly

likely due to this leaving groups affinity for the formation of Gomberg's dimer.

Although this did not occur, complex 4 is an excellent candidate for oxygen atom

transfer experimentation.

Single crystals suitable for x-ray diffraction of complex 4 were obtained

and solved verifying the connectivity of the square planar cobalt (II) metal center

(Figure 2.6). Compound 4 has a Co-O bond length of 1.85 Å and Co-O-C angle

of 138.45° which can be compared to Power's known cobalt alkoxides.[21]

Co(OCPh$_3$)$_2$(THF)$_2$ has a Co-O bond length of 1.872(2) Å and a Co-O-C bond

angle of 129.6(2) °. Two similar complexes [Co(OC(C$_6$H$_{11}$)$_3$)$_2$]$_2$ and [Co-

(OCPh$_2$]$_2$·n-C$_6$H$_{14}$ {(Co-O 1.798(4), 1.763(5) Å and Co-O-C 145.2(5), 158.1(5)

°), and (Co-O 1.814(4), 1.811(4) Å; Co-O-C 137.1(4), 129.4(4) °) show very little

deviation from complex 4.

Table 2.4 Selected bond lengths (Å) and angles (°) for (PNP)Co(OCPh$_3$)

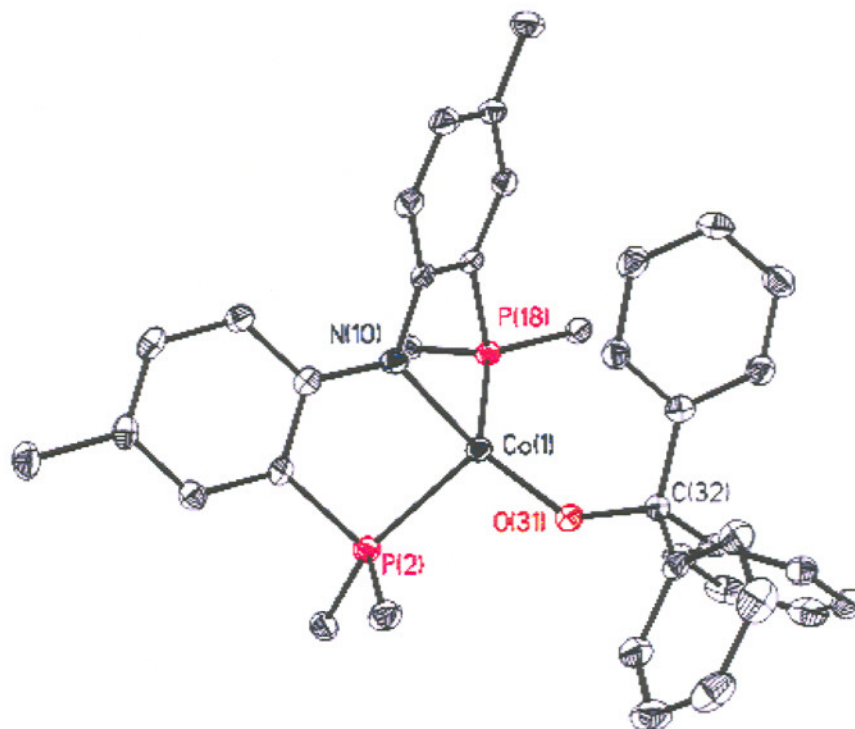|			
Co(1)-O(31)	1.8500(15)	O(31)-Co(1)-N(10)	140.52(7)
Co(1)-N(10)	1.9649(17)	O(31)-Co(1)-P(2)	96.21(5)
Co(1)-P(2)	2.3557(6)	N(10)-Co(1)-P(2)	84.41(5)
Co(1)-P(18)	2.4151(6)	O(31)-Co(1)-P(18)	125.77(5)
		N(10)-Co(1)-P(18)	80.02(5)
		P(2)-Co(1)-P(18)	128.74(2)
		Co(1)-O(31)-C(32)	138.45(13)

Figure 2.6 Molecular structure of 4 with thermal ellipsoids at the 50%
probability level. (^{i}Pr's and H's have been omitted for clarity).

2.7 Synthesis of (PNP)Co(CO)$_2$ (5)

In pursuit of a (PNP)Co=O complex reaction of 4 with carbon monoxide

rapidly formed (PNP)Co(CO)$_2$. Interestingly, formation of 5 resulted in the

radical displacement of Gomberg's dimer (dimerization of the CPh$_3$ radical)

which was confirmed by ^{1}H NMR (Figure 2.7). Upon formation of this dimer and

the reaction of 1 atm of carbon monoxide (Scheme 2.6), complex 4 must form a

cobalt oxo complex.

The molecular structure of this complex was obtained by room

temperature evaporation of deuterated benzene (Figure 2.8) which further

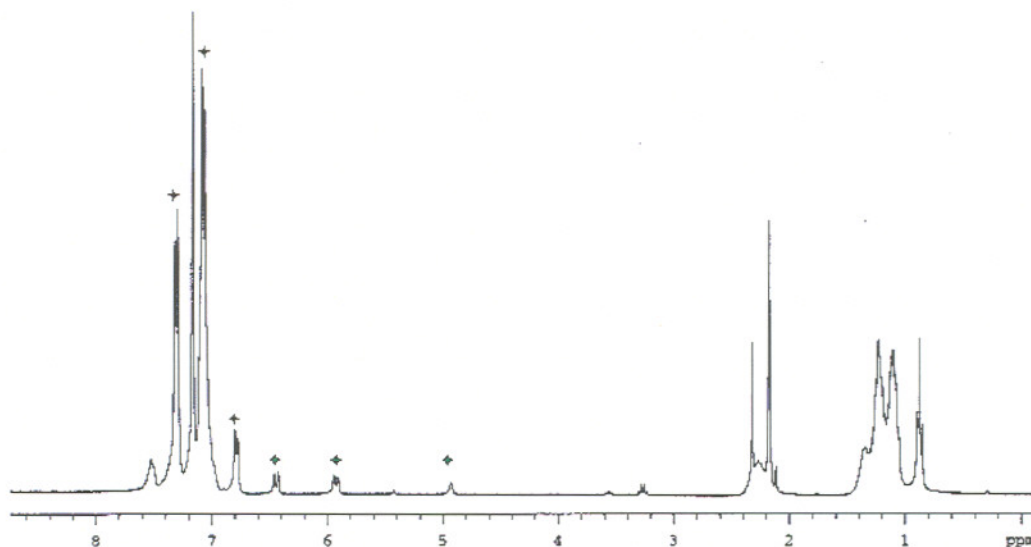confirmed the presence of two carbonyls. The cobalt metal center is in a slightly
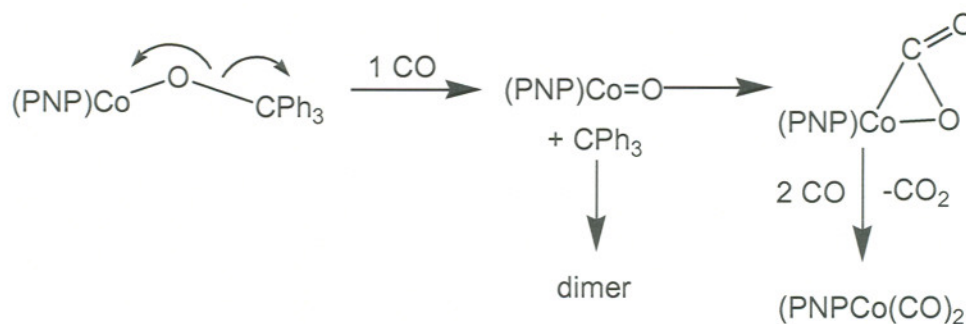
Figure 2.7 ^{1}H NMR of crude (PNP)Co(CO)$_2$, (* indicate Gomberg's dimer).

Scheme 2.6 Synthesis of(PNP)Co(CO)$_2$.

distorted trigonal bipyramidal environment, and selected bond lengths and angles

are given in Table 2.6. Comparison of (PNP)Co(CO)$_2$ to the akin trigonal

bipyramidal cobalt (I) complex, Co(CO)$_2$(PMe$_3$)$_2$(N$_3$)[22], with a Co-CO bond

lengths of 1.739(6), 1.749(5) Å and a CO bond lengths of 1.134(5), 1.145(6) Å
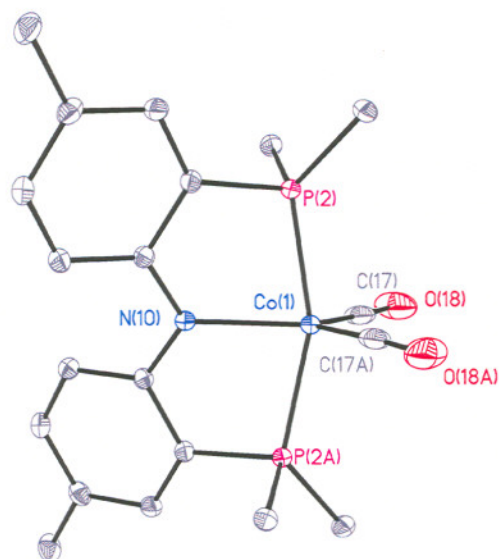
demonstrates no significant variation.[18]

Figure 2.8 Molecular structure of 5 with thermal ellipsoids at the 50% probability level. (^{i}Pr's and H's have been omitted for clarity).

Table 2.5 Selected bond lengths (Å) and angles (°) for (PNP)Co(CO)$_2$

Co(1)-C(17)	1.7556(2)	C(17A)-Co(1)-C(17)	117.35(1)
Co(1)-C(17A)	1.7556(2)	C(17A)-Co(1)-N(10)	121.32(6)
Co(1)-N(10)	2.0346(2)	C(17A)-Co(1)-P(2)	98.25(5)
Co(1)-P(2)	2.2019(4)	C(17)-Co(1)-P(2)	92.405)
Co(1)-P(2A)	2.2019(4)	N(10)-Co(1)-P(2)	79.725(1)
C(17)-O(18)	1.142(2)	P(2)-Co(1)-P(2A)	159.45(2)

Experimental Section

3.1 Synthesis of (PNP)CoCl (1)

A cold solution (-35 °C) of Li(PNP) (1.49, 0.0115 mol) in THF(50 mL) was added to a stirring cold suspension (-35 °C) of $CoCl_2$ (5.0 g, 0.0115 mol) in THF (250 mL). The reaction mixture was allowed to warm to ambient temperature and stirred for 22 hours and the solvent was removed under reduced pressure. After the addition of toluene (50 mL) the suspension was filter to remove LiCl and the filtrate was concentrated under reduced pressure to ca. 15 mL, and cooled (-35 °C) overnight to produce a dark blue crystalline solid (4.56 g, 76%). Observed Evans magnetic moment: 2.32 μ_B. Complete characterization still in progress.

3.2 Synthesis of [Na₂(thf)₃][(PNP)Co(N₂)] (2)

In a 250 mL Erlenmeyer flask sodium metal (528 mg, 22.98 mmol) was cut and spread on the bottom of the flask, to this THF (30 mL) was added. Napthalene (0.098 g, 0.766 mmol) was dissolved in THF (20mL) and added to the stirring suspension, which immediately turned dark green and was left to stir for 6 hours. (1) (0.400 g, 0.766mmol) was dissolved in THF (150 mL) and added to the flask dropwise over a period of three hours. After stirring for an additional 24 hours, the dark brown suspension was filtered. The filtrate was concentrated under reduced pressure to dryness and the dark brown solid was washed with hexane (30 mL) and filtered. The solid is then dissolved in diethyl ether (15mL) and cooled to obtain dark brown crystals (0.398 g, 73%). Complete characterization still in progress.

3.2   Synthesis of (PNP)Co-N=N-Co(PNP) (3)

A stirred brown solution of 2 (0.100 g, 0.130 mmol) in Et$_2$O (5 mL) was cooled (-35 °C) and treated with a cooled (-35 °C) solution of 1 (0.135 g, 0.260 mmol) in Et$_2$O (10 mL). The resulting dark blue/black solution was stirred for an additional 16 hours the concentrated under reduced pressure to dryness and washed with pentane (10 mL) to remove NaCl. The suspension is filtered and the filtrate is concentrated to dryness resulting in a black solid. NMR data (in C$_6$D$_6$): ^{1}H δ 1.14-1.43 (m, 48 H, CH(CH_3)$_2$), 2.11 (s, 6 H, Me), 2.17 (s, 6 H, Me), 2.29 (brs, 8 H , CH(CH$_3$)$_2$), 6.32 (m, 4 H, Ph), 6.70 (d, ^{1}J$_{H-H}$ = 7.8, 2 H, Ph), 6.96 (s, 2 H, Ph), 7.39 (d, ^{1}J$_{H-H}$ = 7.8, 2 H, Ph), 7.56 (s, 2 H, Ph). ^{31}P δ 50.25 (brs, 2 P, PNP), 57.85 (s, 2 P, PNP). Complete characterization still in progress.

3.4 Synthesis of (PNP)Co(OCPh$_3$) (4)

To a cold (-35 °C) stirring solution of 1 (0.100 g, 0.191 mmol) in THF (10 mL) a cold solution (-35 °C) of NaOCPh$_3$ (0.054 g, 0.191 mmol) in THF (6 mL) was added. After stirring for 24 hours the dark blue solution was concentrated to dryness and washed with pentane (10 mL), filtered to remove NaCl and dried in vacuo to obtain a dark blue solid. Complete characterization still in progress.

3.5 Synthesis of (PNP)Co(CO)$_2$ (5)

In a Jay-young tube 4 (0.020 g) was measure and dissolved in C$_6$D$_6$. To this 1 atm of CO (g) was added turning the dark blue solution an immediate green. NMR data (in C$_6$D$_6$): ^{1}H δ 1.11-1.34 (m, 24 H, CH(CH_3)$_2$), 2.17 (s, 6 H, Me), 2.26 (brs, 2 H , CH(CH$_3$)$_2$), 4.93 (s, 1 H, aliphatic proton), 5.92 (d, ^{1}J$_{H-H}$ = 10.2, 2 H, olefinic protons), 6.44 (d, ^{1}J$_{H-H}$ = 10.2, 2 H, olefinic protons), 7.00-7.31 (m, 25

H, aromatic protons), 7.52 (m, 6 H, PNP). ^{31}P NMR δ 97.78 (s, 2 P, PNP).

Complete characterization still in progress.

Conclusions

Five new complexes of cobalt have been synthesized including both a monomeric and dimeric dinitrogen complex. Activation of dinitrogen produced $[Na_2(thf)_3][(PNP)Co(N_2)]$ which can then be reacted with two equivalents of (PNP)CoCl to produce the dimeric end-on dinitrogen bridged complex (PNP)Co-N=N-Co(PNP) with a partially reduced N_2 moiety.

(PNP)CoCl can also be reacted with $NaOCPh_3$ to produce the triphenlymethoxy cobalt (II) complex, which possibly will be a powerful oxygen atom transfer source. Further reaction of the "Co=O synthon" with CO (g) produced a cobalt (I) complex which undergoes an cobalt-oxo intermediate by transferring the oxygen atom to carbon monoxide forming CO_2. Isolation of the oxo intermediate would no only be the first of its kind, but could also be utilized as a valuable oxygen source in oxygen atom transfer chemistry. All five complexes were characterized by ^1H and ^{31}P NMR and x-ray diffraction, further characterization is in progress.

Future Studies

Given our interest in synthesizing the first cobalt-oxo complex we are currently investigating this possibility while still continuing our activation of dinitrogen research.

1. Reaction of (PNP)Co(OCPH$_3$) with Arduengo carbenes, SO_2, O_2, olefins and mild reductants will help in understanding the capabilities of (PNP)Co(OCPH$_3$) as a dominant oxygen atom transfer reagent.

2. Investigation of the reactivity of $(PNP)Co(CO)_2$ with an azide may produce $(PNP)Co=NR$, the isoelectronic species of $(PNP)Co=O$.

3. Similar to the dimeric $(PNPCo)_2N_2$ complex we are interested in synthesizing a variety of mixed valent dinitrogen complexes by reacting $[Na_2(thf)_3][(PNP)Co(N_2)]$ with $(PNP)FeCl$, $(PNP)NiCl$ and $(PNP)ScCl_2$ (all prepared in our lab).

4. Reactivity of $[Na_2(thf)_3][(PNP)Co(N_2)]$ with an array of small and organic molecules including but not limited to CO_2, O_2, and N_2O may result in the transfer of the N_2 fragment to form more complex organic moieties.

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