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[(TMEDA)Co(NO)$_2$][BPh$_4$]: A versatile synthetic entry point to four and five coordinate {Co(NO)$_2$}^{10} complexes

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This paper is dedicated to Professor Kenneth G. Caulton, for his fundamentally important and useful contributions to inorganic and organometallic chemistry, including the work that facilitated the syntheses described in this paper.

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ABSTRACT

[(TMEDA)Co(NO)$_2$][BPh$_4$] reacts with Group 1 salts of various monoanionic ligands to yield four and five coordinate {Co(NO)$_2$}^{10} complexes. The synthesis of the four coordinate complex of the form [{LX}Co(NO)$_2$] via salt-metathesis reactions of [(TMEDA)Co(NO)$_2$][BPh$_4$] with [{ArNC(Me)CHC(Me)NAr}Li(OEt$_2$)] (Ar = 2,6-di-iso-propylphenyl) is reported. In addition [(TMEDA)Co(NO)$_2$][BPh$_4$] reacts with either KTp* or a suite of cyclopentadienyllithium and cyclopentadienylsodium reagents, to generate the corresponding five coordinate [{L$_2$X}Co(NO)$_2$] complexes ({L$_2$X = C$_5$H$_5$, MeC$_5$H$_4$, Cp*, ^{t}BuC$_5$H$_4$, Ph$_2$CHC$_5$H$_4$, Me$_3$SiC$_5$H$_4$, ^{t}BuMe$_2$SiC$_5$H$_4$, ^{i}Pr$_3$SiC$_5$H$_4$, 1,3-(^{i}Pr$_3$Si)$_2$C$_5$H$_3$ and Tp*). In support of existing precedent, the four coordinate complex is a thermally robust and readily isolable species while five coordinate complexes are thermally unstable transient intermediates that may either undergo dissociation of an NO ligand or be trapped by alkenes to form the corresponding metal dinitrosoalkane complexes. These reactions demonstrate that [(TMEDA)Co(NO)$_2$][BPh$_4$] provides a versatile synthetic entry point to cobalt dinitrosyl complexes and obviates the need for the repeated use of nitric oxide in the preparation of dinitrosoalkane complexes of cobalt.

1. Introduction

The importance of nitric oxide (NO) to biological systems has spurred recent research activity into the properties and reactivity of 1st row transition metal nitrosyl complexes [1]. While many current studies are focused on dinitrosyl iron complexes (DNIC) [1,2,3], due to their potential to mediate reactions involving NO *in vivo*, far less attention has been paid to cobalt dinitrosyl complexes despite the similarities between {Fe(NO)$_2$}^{9} and {Co(NO)$_2$}^{10} complexes [4,5].

Existing monomeric {Co(NO)$_2$}^{10} complexes can be organized into four distinct classes. Where L is a neutral 2-electron ligand and X is a mono-anionic ligand, these complexes can be described as: mono-cationic four-coordinate, [L$_2$Co(NO)$_2$]$^+$ (**I**), neutral four coordinate, [LXCo(NO)$_2$] (**II**), mono-anionic four coordinate, [X$_2$Co(NO)$_2$]$^-$ (**III**) and neutral five-coordinate, [L$_2$XCo(NO)$_2$] (**IV**). While the former four coordinate compounds (**I**–**III**) demonstrate distorted tetrahederal geometry at cobalt and are readily isolable, five coordinate {Co(NO)$_2$}^{10} complexes (**IV**) are transient reactive intermediates which, to date, have only be generated and characterized *in situ* (Fig. 1). Although a number of dimeric and polymeric {Co(NO)$_2$}^{10} complexes are also known, including halide bridged compounds of the form [Co(NO)$_2$(μ-X)]$_n$ (X = Cl, Br, $n = 2$; X = I, $n = \infty$) [6], in the context of the current study, discussion is limited to discrete mono-metallic complexes.

Four coordinate cationic species (**I**) supported by both non-chelating and chelating amine, phosphine, phosphite and alkene ligands have been synthesized and characterized [7]. Many have been the subject of single crystal X-ray diffraction investigations [8]. A number of salts of the form **I** have been shown to exhibit conductivity [7], and the electrochemistry of [{(EtO)$_3$P}$_2$Co(NO)$_2$][BF$_4$] has been studied [9]. In an example of applied reaction chemistry, [L$_2$Co(NO)$_2$]$^+$X$^-$ (L = MeCN, PhCN, Me$_2$CO; L$_2$ = COD, norbornadiene; X = PF$_6$, BF$_4$, ClO$_4$) have been reported by Tkatchenko and co-workers to be pre-catalysts for the oligomerization of butadiene, norbornadiene, styrene, isoprene and phenylacetylene [10].

In the 1970s neutral four-coordinate complexes, [(acac)Co(NO)$_2$] (**II**, acac = acetylacetonate) and [(sacsac)Co(NO)$_2$] (**II**, sacsac = dithioacetylacetonate) were synthesized by salt-

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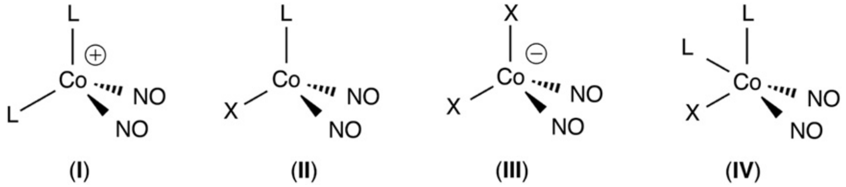


Fig. 1. Monomeric dinitrosyl complexes of cobalt.

metathesis of $[Co(NO)_2Br]_2$ with lithium acetylacetonate and reaction of $[(sacsac)_2Co]$ with nitric oxide respectively [11,12]. More recently Lippard and co-workers have reported not only a four coordinate dinitrosyl) cobalt complex supported by an amino (tropiminate) ligand in the context of nitric oxide sensing but also the β-diketiminate stabilized complex $[\{ArNC(Me)CHC(Me)NAr\}Co(NO)_2]$ (Ar = 2,6-di-*iso*-propylphenyl) [13,4c]. In addition to these studies, a number of phosphine stabilized mono-halide dinitrosyl complexes have been reported [14,15]. Thus Aresta, Tkatchenko and co-workers have reported the synthesis of $[\{PhP(OCH_2CH_2)_2NH\}Co(NO)_2Cl]$ and its reversible reaction with CO_2 [14], while both $[\{(Ph_2P{=}O)CH_2CH_2PPh_2\}Co(NO)_2I]$ and $[(Ph_3P)Co(NO)_2I]$ have been studied by single crystal X-ray diffraction [15].

Lippard and co-workers detailed the synthesis of an anionic $\{Co(NO)_2\}^{10}$ complex of the form **III** in 2008 [4b]. As part of a wider study on biologically relevant dinitrosyl iron complexes, the reaction of $[(PhS)_4Co][Et_4N]_2$ with NO was reported to yield $[(Ph_2S)_2Co(NO)_2][Et_4N]$. While this work was pre-dated by a report of the preparation of $[(NC)_2Co(NO)_2][Na]$ in 1970 [16], characterization data on the latter complex did not include an X–ray diffraction study.

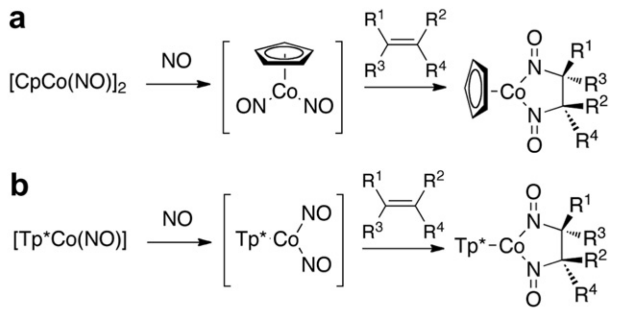
In an unusual example of ligand-based reactivity, Brunner and Loskot reported that the reaction of $[CpCo(\mu\text{-}NO)]_2$ with NO and strained alkenes yielded the corresponding dinitrosoalkane adducts (Scheme 1a) [17]. The scope was expanded and mechanism of this reaction elucidated in subsequent studies from one of our groups [18]. Consistent with the concerted addition of a five coordinate reactive intermediate of the form **IV** to the alkene, binding of the unsaturated substrate was shown to be reversible and stereospecific. Despite being air-sensitive and thermally unstable, $[CpCo(NO)_2]$ (**1**) could be observed by NMR, UV–vis and infrared spectroscopy at low concentrations in solution. It is noteworthy that **1** may act as a *stoichiometric* reagent for not only alkene diamination, but also for the C–H functionalization of strained alkenes through base-mediated reactions with Michael acceptors [19]. More recently, we have found that $[Tp^*Co(NO)]$ may be synthesized *via* a salt-metathesis reaction between KTp^* and $[(TMEDA)Co(NO)_2][BPh_4]$ (**2**) in THF solution [20]. Under a pressure of NO, the former complex forms an equilibrium mixture with the corresponding five-coordinate species $[Tp^*Co(NO)_2]$ which in turn may be trapped as the dinitrosoalkane adduct by addition to norbornene (Scheme 1b).

We now report the synthesis and characterization of a number of four and five-coordinate $\{Co(NO)_2\}^{10}$ complexes, by salt-metathesis reactions of $[(TMEDA)Co(NO)_2][BPh_4]$ with various mono-anionic ligands, along with their reactions with alkenes. In line with the expectations provided by existing studies (*vide supra*), while a hydrocarbon soluble four coordinate system is thermally robust and unreactive with alkenes and alkynes up to 100 °C, five coordinate species are transient intermediates that readily bind alkenes at temperatures as low as −78 °C. In the absence of an alkene trap the five coordinate species readily dissociate NO.

2. Experimental

2.1. General experimental

Unless otherwise indicated, operations were performed under anhydrous conditions and inert atmosphere employing standard Schlenk-line and glovebox techniques. Glassware was dried in an oven at 160 °C overnight or flame-dried prior to use. NMR spectra were acquired using Bruker AV-300, AVQ-400, AVB-400 and AV-500 spectrometers. Chemical shifts are reported as part per million (ppm, δ) and ^1H and ^{13}C chemical shifts are referenced to the corresponding residual protic solvent resonance. All mass spectra (LR-MS and HR-MS) were recorded at the University of California, Berkeley Microanalytical Facility with electrospray ionization (ESI) or fast atom bombardment techniques (FAB) in positive mode. Fast atom bombardment mass spectra were recorded on a Micromass ZAB2-EQ magnetic sector instrument. Infrared spectral data were recorded on a Thermo Scientific Nicolet iS10 spectrometer fitted with a Smart OMNI-transmission or Smart iTR device as either KBR discs, neat solids or thin films. Elemental analyses were recorded by the UC Berkeley micro-mass facility. Thin layer chromatography was performed using 0.25 mm precoated silica gel plates from Silicycle containing a fluorescent indicator for visualization by UV light. Flash chromatography was performed using MP Biomedicals SiliTech silica gel 32–63D, 60 Å. Solvents were dried through a push-still system *via* passage through activated alumina. Cobalt(II) chloride was dried prior to use by heating under vacuum (120 °C at 1×10^{-1} mbar) for 12 h. Volatile alkenes were distilled from calcium hydride and freeze-pump-thaw de-gassed prior to use. 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene [21] was synthesized by the literature procedure. NO gas was purified by passage through a −78 °C trap before use. The cobalt complex **2** was synthesized by a modification of the procedure reported by Caulton and co-workers [7a]. The lithium salts $[\{ArNC(Me)CHC(Me)NAr\}Li(OEt_2)]$ (Ar = 2,6-di-*iso*-propylphenyl), $[Li(^tBuC_5H_4)]$, $[Li\{(Ph_2CH)C_5H_4\}]$, $[Li(C_5H_4SiMe_3)]$, $[Li\{C_5H_4(Si^tBuMe_2)\}]$, $[Li\{(Si^iPr_3)C_5H_4\}]$ and $[Li\{1,3\text{-}(^iPr_3Si)_2C_5H_3\}]$ were prepared by literature procedures [22,23],



Scheme 1. Representative alkene binding reactions of (a) $[CpCo(NO)]_2$/NO and (b) $[Tp^*Co(NO)]$/NO.