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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 $[\{L_2X\}Co(NO)_2]$ complexes ($\{L_2X = C_5H_5, MeC_5H_4, Cp^*, {}^tBuC_5H_4, Ph_2CHC_5H_4, Me_3SiC_5H_4, {}^tBuMe_2SiC_5H_4, {}^iPr_3SiC_5H_4, 1,3\text{-}({}^iPr_3Si)_2C_5H_3$ 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, $[L_2Co(NO)_2]^+$ (**I**), neutral four coordinate, $[LXCo(NO)_2]$ (**II**), mono-anionic four coordinate, $[X_2Co(NO)_2]^-$ (**III**) and neutral five-coordinate, $[L_2XCo(NO)_2]$ (**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 $[Co(NO)_2(\mu\text{-}X)]_n$ (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 $[\{(EtO)_3P\}_2Co(NO)_2][BF_4]$ has been studied [9]. In an example of applied reaction chemistry, $[L_2Co(NO)_2]^+X^-$ (L = MeCN, PhCN, Me_2CO; 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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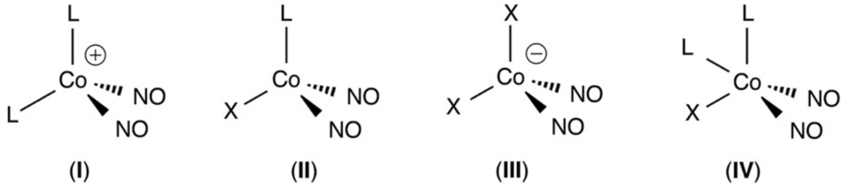


Fig. 1. Monomeric dinitrosyl complexes of cobalt.

metathesis of [Co(NO)$_2$Br]$_2$ with lithium acetylacetonate and reaction of [(sacsac)$_2$Co] 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$_2$CH$_2$)$_2$NH}Co(NO)$_2$Cl] and its reversible reaction with CO$_2$ [14], while both [{(Ph$_2$P=O)CH$_2$CH$_2$PPh$_2$}Co(NO)$_2$I] and [(Ph$_3$P)Co(NO)$_2$I] 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)$_4$Co][Et$_4$N]$_2$ with NO was reported to yield [(Ph$_2$S)$_2$Co(NO)$_2$][Et$_4$N]. While this work was pre-dated by a report of the preparation of [(NC)$_2$Co(NO)$_2$][Na] in 1970 [16], characterization data on the latter complex did not include an X–ray diffraction study.

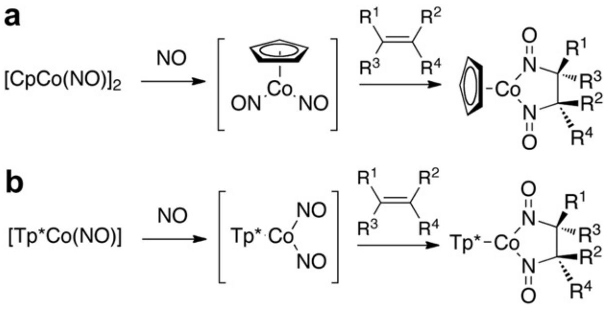
In an unusual example of ligand-based reactivity, Brunner and Loskot reported that the reaction of [CpCo(μ-NO)]$_2$ with NO and strained alkenes yielded the corresponding dinitrosoalkane adducts (Scheme 1a) [17]. The scope was expanded and mechanism of this reaction elucidated in subsequent studies from 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(^{t}BuC$_5$H$_4$)], [Li{(Ph$_2$CH)C$_5$H$_4$}], [Li(C$_5$H$_4$SiMe$_3$)], [Li{C$_5$H$_4$(Si^{t}BuMe$_2$)}], [Li{(Si^{i}Pr$_3$)C$_5$H$_4$}] and [Li{1,3-(^{i}Pr$_3$Si)$_2$C$_5$H$_3$}] 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.

Table 1
X-ray experiment acquisition parameters and selected data on compounds **2** and **4j**.

	2	**4j**
Molecular formula	$C_{30}H_{36}BCoN_4O_2$	$C_{23}H_{34}BCl_2CoN_8O_2$
Formula weight (g mol^{-1})	554.37	595.22
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	P–1
a (Å)	21.083(2)	10.7950(12)
b (Å)	9.6623(9)	11.2263(13)
c (Å)	14.0373(13)	12.6478(15)
α (deg)	90	102.699(2)
β (deg)	90	93.487(2)
γ (deg)	90	110.050(2)
V (Å^3)	2859.5(5)	1389.0(3)
Z	4	2
μ (mm^{-1})	0.633	0.847
ρ (g cm^{-3})	1.288	1.423
θ range (o)	2.32–30.99	1.67–25.33
R_1[a] wR_2[b] [$I > 2\sigma(I)$]	0.0272, 0.0686	0.0362, 0.0909
R_1[a] wR_2[b] (all data)	0.0326, 0.0722	0.0423, 0.0960
Measured/independent reflections/R_{int}	81294/9063/0.0444	7783/4524/0.0204

[a] $R_1 = \Sigma\ ||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR2 = \{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^{2)2}]\}^{1/2}$

while [KTp*] was purchased from Sigma–Aldrich and used without further purification. All other reagents were obtained from commercial suppliers (Aldrich, Strem) and used without further purification. Full characterization data for compounds **4a**–**q** are presented in the supporting information.

2.2. Acquisition of X-ray data

Single crystal X-ray diffraction experiments for compound **4j** were conducted at UC Berkeley CheXray facility using a SMART APEX diffractometer equipped with a fine-focus sealed tube, Mo K/α source, and Bruker APEX-I CCD detector. A multi-scan absorption correction was applied, while structures were solved with SIR-2004 and refined in SHELXL-97 [24]. Selected acquisition data are presented in Table 1. CIF files for compounds **2** and **4j** were deposited in the CCDC database and are assigned as CCDC 815248 and 815249 respectively.

2.3. Synthetic procedures

*2.3.1. Synthesis of [{ArNC(Me)CHC(Me)NAr}Co(NO)$_2$] (Ar = 2,6-di-iso-propylphenyl) (**3**)*

In a glovebox, [(TMEDA)Co(NO)$_2$][BPh$_4$] (306 mg, 0.552 mmol) and [{ArNC(Me)CHC(Me)NAr}Li(OEt$_2$)] (275 mg, 0.552 mmol) were weighed out separately and transferred to a Schlenk vessel. The vessel was sealed, removed from the box and attached to a Schlenk line. After toluene (5 ml) was added the sealed vessel was heated to 80 °C for 4 days. Lithium tetraphenylborate may be removed by filtration following evaporation of solvent and extraction of the crude reaction mixture in to hexanes. Removal of the solvent and crystallization gave the product as a brown solid (179 mg, 0.334 mmol, 60%). X–ray quality crystals were obtained from slow evaporation of a concentrated pentane solution. ^{1}H NMR (d_8-tol, 300 MHz, 298 K) 1.14 (d, 12H, J = 6.9 Hz), 1.21 (d, 12H, J = 6.9 Hz), 1.73 (s, 6H), 3.11 (hept, 4H, J = 6.9 Hz), 5.13 (s, 1H), 6.98–7.10 (m, 6H); ^{13}C NMR (d_8-tol, 100 MHz, 298 K) 23.2, 24.6, 24.8, 27.6, 100.8, 124.0, 126.1, 142.6, 148.4, 164.2; Infrared (KBr disc, cm^{-1}) 2960, 2925, 2866, 1807, 1721, 1525, 1400; LR-MS (FAB, +ve ion) 536 ([M]$^+$, 10%), 506 ([M–NO]$^+$, 100%), 476 ([M–2NO]$^+$, 50%). Data match those reported by Lippard and co-workers [4c].

*2.3.2. Representative procedure for the synthesis of cobalt dinitrosoalkane complexes of norbornene (**4a–j**)*

Under an inert atmosphere, a solution of the group 1 complex (0.54 mmol, 1.2 equiv., see Table 3 for details) in THF (10 mL) was added *via* cannula to a slurry of [(TMEDA)Co(NO)$_2$][BPh$_4$] (250 mg, 0.45 mmol, 1 equiv.) and norbornene (4.5 mmol, 10 equiv.) in THF (10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for several hours or overnight (see Table 3 for details). The reaction could be monitored by analysis of aliquots by thin layer chromatography on silica gel (3:1 hexanes/ethyl acetate eluent). Once the reaction was complete, the THF was removed *in vacuo* and the crude product dissolved in minimal methylene chloride and purified on silica gel using a 9:1 mixture of hexanes:ethyl acetate as the eluting solution. Products isolated in this manner proved air- and moisture stable in the solid state and could be handled on the bench-top. While full characterization details are given in the supporting information, as an example the data for **4f** are the following: Black solid (0.149 g, 0.39 mmol, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) 5.15 (s, 2H), 4.73 (s, 2H), 2.68–2.69 (m, 2H), 2.60–2.61 (m, 2H), 1.45–1.51 (m, 1H), 1.16–1.18 (m, 2H), 0.85–0.87 (m, 1H), 0.85 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K) 95.8, 94.2, 93.7, 92.9, 42.2, 30.9, 26.3, 26.2, 17.1, −5.9; Infrared (solid, cm^{-1}) 2953, 2926, 2855, 1403, 1357, 1352, 1265, 1251;; m/z (FAB, +ve ion) 393 (100%, [M + H]$^+$), 335 (55%, [M+H–C$_4$H$_9$]$^+$); HR-MS (ESI, +ve) for $C_{18}H_{30}O_2N_2CoSi$ 393.1403 found 393.1387.

2.3.3. Representative procedure for the synthesis of tris(pyrazolyl) borate dinitrosoalkane complexes

Under an inert atmosphere, a solution of [KTp*] (72.6 mg, 0.216 mmol, 1.2 equiv.) in THF (10 mL) was added *via* cannula to a slurry of **2** (100 mg, 0.181 mmol, 1 equiv.) and alkene (1.81 mmol, 10 equiv.) in THF (10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction could be monitored by analysis of aliquots by thin layer chromatography on silica gel. Once complete the THF was removed *in vacuo* and the crude product dissolved in minimal methylene

Table 2
Selected bond angles (°) and bond lengths (Å) of selected four coordinate {Co(NO)$_2$}^{10} complexes.

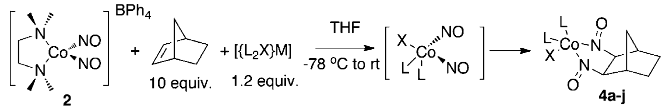
	2	[(py)$_2$Co(NO)$_2$][BF$_4$] [8c]	**3**[a]	[(PhS)$_2$Co(NO)$_2$] [Et$_4$N] [4b]
Co–N	1.6630(12)	1.654(6)	1.645(4), 1.649(4)	1.651(3)
	1.6636(12)	1.644(6)	1.690(4), 1.693(4)	1.684(3)
N–O	1.1475(16)	1.130(8)	1.161(4), 1.154(4)	1.106(3)
	1.1582(15)	1.156(8)	1.174(5), 1.169(5)	1.126(3)
N–Co–N	112.77(7)	115.6(3)	110.4(2), 110.9(2)	110.35(14)
Co–N–O	168.53(13)	170.2(6)	171.6(4), 174.3(4)	174.9(2)
	165.83(11)	170.1(6)	148.5(4), 150.3(4)	161.4(3)
Co–X[b]	2.0423(12)	2.012(6)	1.963(4), 1.970(4)	2.2565(8)
	2.0652(12)	2.012(6)	1.956(4), 1.961(4)	2.2478(8)

[(py)$_2$Co(NO)$_2$]$^+$BF$_4$ and **3** X = N and for [(PhS)$_2$Co(NO)$_2$]Et$_4$N X = S.

[a] Data are within experimental error of those independently reported by Lippard and co-workers [4c].

[b] X represents the heteroatoms of the neutral or mono-anionic supporting ligands, for **2**.

Table 3
Scope of the reaction of **2** with cyclopentadienyl and *tris*(pyrazolyl)borate anions in the presence of norbornene.



$[\{L_2X\}M]$	Complex	Reaction time	Yield[a]
[NaCp]	**4a**	4h	57%
$[Li\{\eta^5\text{-}MeC_5H_4\}]$	**4b**	12h	66%
$[LiCp^*]$	**4c**	12h	67%
$[Li\{\eta^5\text{-}{}^tBuC_5H_4\}]$	**4d**	0.5h	74–94%
$[Li\{\eta^5\text{-}(Ph_2CH)C_5H_4\}]$	**4e**	4h	31%
$[Li\{\eta^5\text{-}Me_3SiC_5H_4\}]$	**4f**	0.5h	75%
$[Li\{\eta^5\text{-}{}^tBuMe_2SiC_5H_4\}]$	**4g**	0.5–12h	63–93%
$[Li\{\eta^5\text{-}{}^iPr_3SiC_5H_4\}]$	**4h**	12h	63%
$[Li\{\eta^5\text{-}1,3\text{-}({}^iPr_3Si)_2C_5H_3\}]$	**4i**	12h	86%
$[KTp^*]$	**4j**	12h	65%[b]

[a] Reactions were conducted at 0.2 M in alkene, by addition of a solution of the anion salt (1.2 equiv.) in THF to a solution of **2** and norbornene (10 equiv.) in THF at −78 °C. Following addition reaction mixtures were warmed to room temperature and stirred for the specified time.

[b] Alkene concentration was 0.1 M.

chloride and purified on silica gel using a 9:1 mixture of hexane:ethyl acetate as the elutent. Products isolated in this manner proved air and moisture stable in the solid state and could be handled on the bench-top. While full characterization details are given in the supporting information, as an example the data for **4k** are the following: Brown solid (62.8 mg, 62% yield). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) 1.81 (d, 1H, $J = 9.2$ Hz), 1.89 (s, 9H, *Me*), 2.29 (d, 1H, $J = 9.2$ Hz), 2.34 (m, 2H), 2.39 (s, 9H, *Me*), 3.36 (m, 2H, C*H*NO), 5.79 (s, 3H, Ar*H*), 6.51 (s, 2H, C=C*H*); ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K) 12.6, 13.7, 42.5, 42.7, 92.7, 107.5, 139.1, 145.2, 150.5; Infrared (KBr disc, cm^{-1}) 3050, 2964, 2924, 2505, 1544, 1365, 1341; LR-MS (ESI, +ve ion) 509 (100%, [M$^+$]), HR-MS (ESI, +ve ion) Calc. for $C_{22}H_{31}O_2N_8BCo$ 509.1990 found 509.1982. Elemental analysis calc. for $C_{22}H_{30}O_2BCoN_8$ C, 51.99; H, 5.95 N, 22.05 found C, 52.42; H, 6.04; N, 21.74.

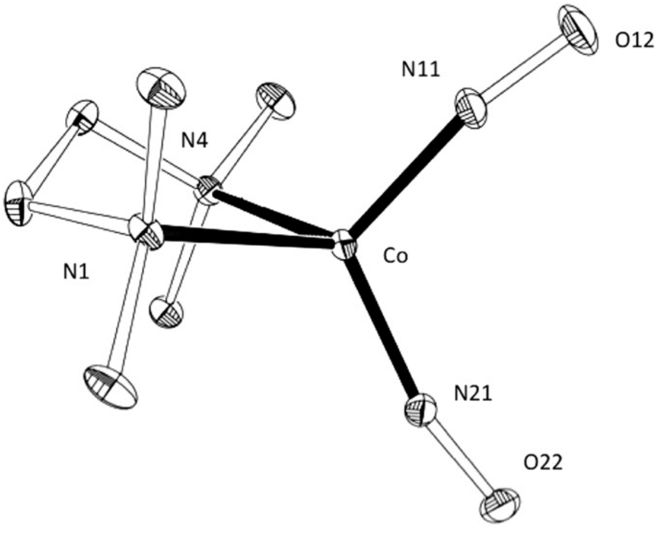


Fig. 2. ORTEP representation of **2** thermal ellipsoids at 20% probability. Protons and the tetraphenylborate anion have been omitted for clarity.

2.3.4. *Synthesis of* $[\{{}^tBuMe_2SiC_5H_4\}Co(\mu\text{–}NO)]_2$

In a glovebox, $[(TMEDA)Co(NO)_2][BPh_4]$ (200 mg, 0.362 mmol, 1 equiv.) and $[Li\{({}^tBuMe_2Si)C_5H_4\}]$ (67.2 mg, 0.362 mmol, 1 equiv.) were weighed into separate vials. A slurry of the cobalt complex was made in THF (4 mL) and a solution of the cyclopentadienyllithium reagent in THF (1 mL) added dropwise. The reaction mixture was stirred for 0.5 h at room temperature and the solvent removed under vacuum. The crude product was extracted with 10 mL of benzene and flushed through a short silica pad (5 cm depth × 4 cm diameter) eluting with benzene (40 mL). The resultant black-green solution was evaporated to dryness to give the product $[\{Me_2{}^tBuSiC_5H_4\}Co(\mu\text{–}NO)]_2$ as a black solid (31.2 mg, 0.058 mmol, 32%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 298 K) 5.32 (m, 4H), 4.97 (m, 4H), 0.80 (s, 18H), 0.14 (s, 12H); ^{13}C NMR (toluene-d^8, 100 MHz, 298 K) 94.7, 89.6, 26.1, 1.0, −5.9; Infrared (solid, cm^{-1}) 2924, 2852, 1588, 1533, 1468, 1247; LR-MS (EI, +ve ion) 536 (60%, [M$^+$]).

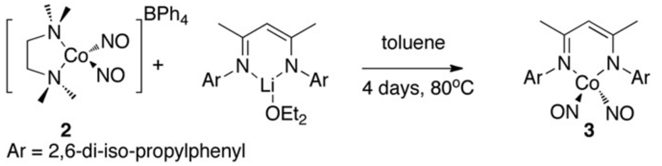
3. Results and discussion

3.1. *Four-coordinate* $\{Co(NO)_2\}^{10}$ *complexes*

In accordance with the procedure reported by Caulton and coworkers, [7a–b] the reaction of CoCl$_2$, two equivalents of tetramethylethylenediamine (TMEDA) and NO in dry methanol followed by addition of NaBPh$_4$ allowed isolation of a mixture of $[(TMEDA)Co(NO)_2][BPh_4]$ (**2**) and [TMEDA•H][BPh$_4$]. Crystallizing in the orthorhombic space group Pna2$_1$, compound **2** is represented in Fig. 2. Although insoluble in hydrocarbon solvents, compound **2** is partially soluble in THF and has proven a versatile synthetic entry point into dinitrosyl cobalt chemistry through salt-metathesis reactions.

Compound **2** readily reacts with [{ArNC(Me)CHC(Me)NAr}Li•OEt$_2$] (Ar = 2,6-di-*iso*-propylphenyl) Scheme 2 in toluene solution at 80 °C to yield $[\{ArNC(Me)CHC(Me)NAr\}Co(NO)_2]$ (**3**). The reaction takes place with displacement of TMEDA from the coordination sphere of **2** and elimination of LiBPh$_4$. The black complex **3** isolated in this manner proved exceptionally soluble in hydrocarbon solvents and must be handled under an anaerobic atmosphere. Despite this, under nitrogen or argon, **3** is thermally robust and may be heated at 100 °C in toluene for up to 24 h without notable decomposition. Lippard and co-workers have recently reported the synthesis of **3** from a similar salt-metathesis reaction employing $[Co(NO)_2(\mu\text{–}Cl)]_2$ in the place of **2** and provided single crystal X-ray diffraction data on this complex [4c].

For comparison, the solid state data for the cationic complexes $[(py)_2Co(NO)_2][BF_4]$ and **2** are presented alongside those of **3** and the related anionic complex $[(PhS)_2Co(NO)_2][Et_4N]$ (Table 2) [4b,8c]. To date all four-coordinate $\{Co(NO)_2\}^{10}$ complexes reported display distorted tetrahedral geometry at the metal and compound **2** follows this trend. While comparison of cobalt-nitrogen bond lengths to the supporting ligand in the cationic complexes **2** and $[(py)_2Co(NO)_2][BF_4]$ (2.0423(12) and 2.012(6) Å respectively) to those in **3** (1.956(4) and 1.961(4) Å) reveals a substantial shortening of the bond distances from cobalt to the mono-anionic LX-type



Scheme 2. Reaction of **2** with [{ArNC(Me)CHC(Me)NAr}Li(OEt$_2$)] (Ar = 2,6-di-iso-propylphenyl) in toluene solution.

ligand relative to L_2-type ligands, comparison of the bonding parameters in the $\{Co(NO)_2\}^{10}$ fragment is more complicated. Descriptions of the bonding subtleties of $\{Co(NO)_2\}^{10}$ complexes have been the subject of a previous discussion [12]. While cobalt-nitrogen bond lengths of the nitric oxide ligands lie in the expected range of 1.61–1.73 Å [12], the lengthening of the nitrogen-oxygen bond lengths in **3** (1.154(4)–1.174(5) Å) relative to those found in **2** (1.1475(16)–1.1582(15) Å) occurs concomitantly with the bending of the M–N–O angles from linearity (**2**, 165.83(11)–168.53(13)°; **3**, 148.5(4)–174.3(4)°) and a compression of the N(1)–M–N(2) angle (**2**, 112.77(7); **3**, 110.4(2) and 110.9(2)). The distortion of the bond lengths and angles of the metal nitrosyl ligands in **3** relative not only to the cationic complexes **2** and $[(py)_2Co(NO)_2][BF_4]$, but also the anionic complex $[(PhS)_2Co(NO)_2][Et_4N]$, is notable (Table 2) [4b,8c]. While interpretation of these solid-state data should be approached cautiously, due to possible crystal packing effects, the increased deviation from linear bonding modes of nitric oxide in **3** could be explained in terms of increased π-back donation to NO arising from increased electron density on the metal due to more efficient π-donation from the β-diketiminate ligand.

Examination of infrared spectroscopy data for four-coordinate $\{Co(NO)_2\}^{10}$ complexes provides additional support for this hypothesis. Compound **3** displays asymmetric and symmetric N–O stretches at 1807 and 1721 cm^{-1} respectively in the solid state, data that compare well to those reported by Lippard and co-workers in C_6D_6 solution (1801 and 1706 cm^{-1}) [4c] These absorptions lie slightly outside the ranges established for compounds of the type **II** (ν_{asym} = 1876–1820 cm^{-1} and ν_{sym} = 1798-1750 cm^{-1}) and are consistent with a degree of back donation from the diketiminate ligand increasing the electron density on the metal. The anionic complex $[(PhS)_2Co(NO)_2][Et_4N]$ reported by Lippard and co-workers displays v(NO) stretches at 1756 and 1678 cm^{-1} in the solid-state. Despite this complex possessing shorter N–O bond lengths than **3** it displays only a minor perturbation of M–N–O bond angles from idealized linear geometry in the reported solid-state structure (Table 2) [4b].

Heating samples of **2** in the presence of 10 equiv. of norbornene in THF in a sealed vessel over 14 h at 75 °C provided no evidence for new organometallic species derived from alkene binding to **2**. The low solubility of **2** even in coordinating polar solvents, however, prevented a detailed study of its chemistry with unsaturated substrates. Thus, the reactions of **3** with cyclopentene, norbornene, diphenylacteylene, isoprene or *trans,trans*-1,4-butadiene in either d^8-toluene or C_6D_6 solution were monitored by ^1H NMR spectroscopy. In all instances no reaction was observable up to temperatures of 100 °C over 12–48 h with starting materials remaining. These results contrast dramatically to those found when generating five coordinate $\{Co(NO)_2\}^{10}$ complexes from **2** by reaction with LiCp or KTp* anions (*vide infra*), and while it may be argued that **3** posses a sterically protected metal center, the ligand-based reaction was expected to occur at the periphery of the coordination sphere. Current data, however, cannot rule out the possibility that four coordinate $\{Co(NO)_2\}^{10}$ complexes could coordinate alkenes to the nitrosyl ligands.

3.2. Five-coordinate $\{Co(NO)_2\}^{10}$ complexes

The reaction of **2** with NaCp in THF (10 mM) at room temperature gave an immediate color change from brown to bright green and the generation of $[CpCo(NO)_2]$ (**1**) could be monitored by react-IR spectroscopy *via* the appearance of NO stretches at 1692 and 1611 cm^{-1} [18]. Performing the reaction of **2** with a variety of substituted cyclopentadienyl salts at −78 °C in THF in the presence of 10 equiv. of norbornene provided facile access to the corresponding dinitrosoalkane complexes (**4a**–**i**, Table 3). In these reactions **2** acts as a convenient source of "$[Co(NO)_2]^+$" obviating the need to repeatedly use nitric oxide gas in the preparation of cobalt dinitrosyl) complexes [17–19]. Furthermore, **2** may be conveniently prepared on a multi-gram scale providing a useful starting material for synthetic diversification. The reaction products **4a**–**i** proved air and moisture stable and were purified by flash column chromatography on the bench-top.

While the reaction of **2** with a series of cyclopentadienyl salts led to the generation and trapping of a number of $[CpCo(NO)_2]$ derivatives, of more interest was the possibility to introduce new ligand sets on cobalt through reaction with alternative metal salt precursors. *Tris*(pyrazolyl)borate ligands have long been considered as surrogates for cyclopentadienyl ligands [25–28], and the reaction of **2** with potassium *tris*(3,5-dimethylpyrazolyl)borate in the

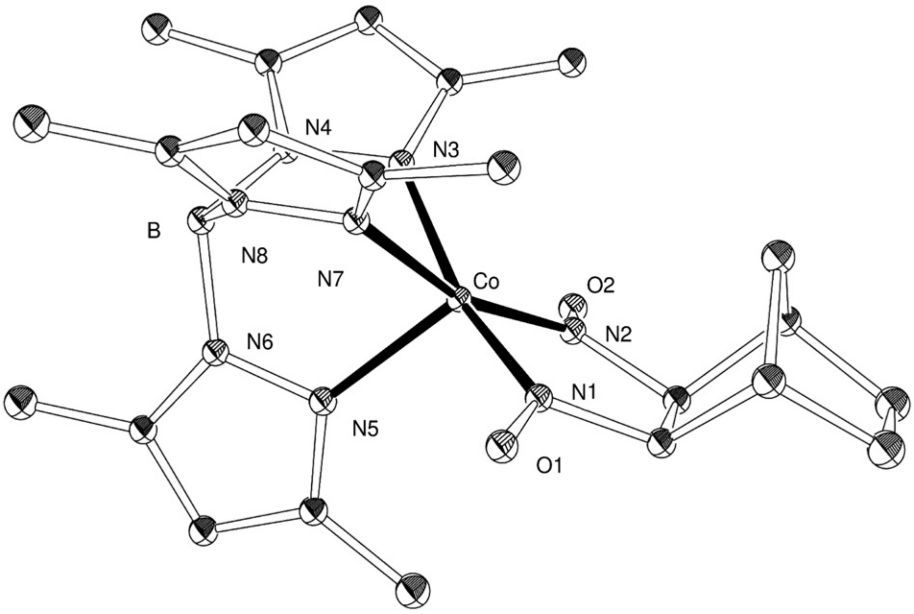


Fig. 3. ORTEP representation of **4j**, thermal ellipsoids at 20% probability H-atoms of omitted for clarity.

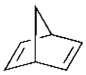
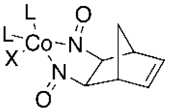
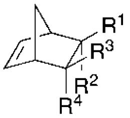
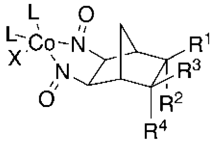
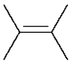
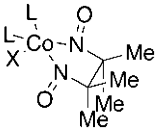
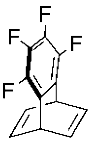
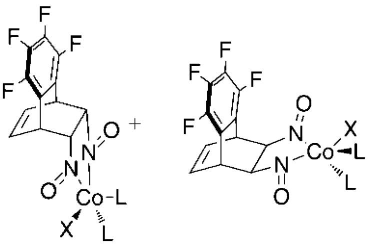
Table 4
Selected bond angles (o) and bond lengths (Å) for **4j**, [CpCo{(μ-NO)$_2$(C$_7$H$_{10}$)}], [Tp^{iPr,Me}Co(CO)$_2$] and [Tp*Co(NO)].

	[Tp^{iPr,Me}Co(CO)$_2$] [28]	[Tp*CoNO] [20]	**4j**	[CpCo{(μ-NO)$_2$(C$_7$H$_{10}$)}] [17c]
Co–N(1)	–	1.625(5)	1.791(2)	1.761(3)
Co–N(2)	–	–	1.793(2)	1.764(3)
N(1)–O(1)	–	1.161(6)	1.256(2)	1.252(4)
N(2)–O(2)	–	–	1.248(3)	1.247(4)
N(1)–C(1)	–	–	1.498(3)	1.492(5)
N(2)–C(2)	–	–	1.504(3)	1.487(5)
N(3)–Co	1.985(8)	2.010(4)	2.0140(19)	–
N(5)–Co	2.087(11)	2.009(3)	2.057(2)	–
N(7)–Co	2.002(12)	–	2.0065(19)	–
N(1)–Co-N(2)	–	–	85.45(9)	87.6(1)
Co–N(1)–O(1)	–	173.5(6)	–	–

presence of 10 equiv. of norbornene in THF at −78 °C followed by warming to room temperature led to the dinitrosoalkane adduct **4j** in 65% yield (Table 3, entry 10). Attempts to observe the reaction intermediate [Tp*Co(NO)$_2$] formed from the reaction of **2** and KTp* in THF at room temperature by react-IR spectroscopy failed and led only to the observation and isolation of the previously reported mono-nitrosyl complex [Tp*Co(NO)] [20].

Single crystals of **4j** were grown by slow diffusion of pentane into a concentrated dichloromethane solution. An ORTEP diagram derived from a single crystal X-ray diffraction experiment is presented in Fig. 3 and selected bond angles and bond lengths are presented in Table 4 along with those of related complexes. In the solid state, the asymmetric unit contains a single molecule of **4j** and methylene chloride. The five-coordinate cobalt center of **4j** possess near perfect square-based pyramidal geometry (Tau factor = 0.04) [29]. Both Co–N and N–O bond lengths of the dinitrosoalkane ligand reflect those reported for the cyclopentadienyl analogue as does the N(1)–Co–N(2) bite angle (Table 4) [17c]. Consistent with the square-based geometry at cobalt the equatorial arms of the *tris*-(pyrazolyl)borate ligand demonstrate closer contacts to the metal centre than the axial ligand (equatorial Co–N(3) 2.015(4) and Co–N(7) 2.005(3) Å; axial Co–N(5) 2.059(4) Å). Similar observations have been made before in *tris*(pyrazolyl)borate chemistry and [Tp^{iPr,Me}Co(CO)$_2$], which also demonstrates a square-based

Table 5
Scope of the reaction of *in situ* generated [{L$_2$X}Co(NO)$_2$] complexes from **2** and [M{L$_2$X}] with alkenes.

[M{L$_2$X}]	Alkene	Product		Yield
[KTp*] [Li{^{t}BuMe$_2$SiC$_5$H$_4$}]		 -	**4k** **4l**	62%[a] 86%[b]
[KTp*] [Li{^{t}BuMe$_2$SiC$_5$H$_4$}] [KTp*]		 R^2=R^4= –(CH$_2$CH=CH)– R^1=R^3=H R^2=R^4= –(CH$_2$CH=CH)– R^1=R^3=H R^1=R^4=CO$_2$Me R^2=R^3=H	**4m** **4n** **4o**	56%[a] 88%[b] 31%[a]
[Li{^{t}BuMe$_2$SiC$_5$H$_4$}]		 -	**4p**	67%[c]
[NaCp]		 -	*endo*- **4q** + *exo*-**4q**	77%[d]

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[a] Reactions were conducted at 0.1 M in alkene, by addition of a solution of the anion salt (1.0–1.2 equiv.) in THF to a solution of 2 and alkene (10 equiv.) in THF at −78 °C. Following addition reactions were warmed to room temperature and stirred overnight.

[b] Alkene concentration was 0.2 M.

[c] The reaction was conducted at rt using 20 equiv. of 2,3-dimethylbut-2-ene (0.2 M), 1 h reaction time.

[d] The reaction mixture was quenched at −78 °C after 0.5 h, 2 equiv. of alkene (0.2 M), 1:1 mixture of endo and exo-isomers.

pyramidal geometry and possesses a cobalt center with an asymmetrically bound *tris*(pyrazolyl)borate ligand (equatorial Co-N 1.985(8) and 2.002(2) Å; axial Co–N 2.087(11) Å) [28].

Despite the apparent C_s-symmetry of complex **4j** in the solid-state, at 298 K in $CDCl_3$, C_6D_6 and d_8-toluene the metal bound pyrazolyl groups are equivalent as observed by ^1H NMR spectroscopy. Variable temperature experiments on **4j** confirmed that this observation was due to fast exchange of the pyrazolyl ligands in the high temperature regime, and cooling of a d_8-toluene solution of **4j** to 193 K revealed decoalescence of both the methyl and methine proton resonances ascribed to the pyrazolyl moieties. Over the same temperature range resonances attributed to the bicyclic hydrocarbon fragment showed no decoalescence behaviour. While the methyl groups of Tp* split into two pairs of resonances consistent with 'freezing-out' of the C_s-symmetric structure observed in the solid state, perhaps most informative was the decoalescence of the methine resonance; this was present as a singlet at 5.60 ppm at 298 K but this signal split into two singlet resonances at 5.70 and 5.77 ppm in a 1:2 ratio on cooling to 193 K. From the coalescence temperature ($T_c = 216 \pm 3$ K) and maximum peak separation ($\Delta\nu = 38 \pm 2$ Hz) the activation energy of the interconversion process may be calculated as $\Delta G^\dagger = 10.6 \pm 0.2$ kcal mol^{-1}. Although the process describes the interconversion of the axial and equatorial pyrazolyl ligands of the face-capping Tp* ligand, it remains possible that this interconversion occurs *via* either (*i*) ligand dissociation, bond rotation and ligand association or (*ii*) a Berry *pseudo*-rotation. The current data cannot discriminate between these mechanisms.

The binding of a number of alkenes to the putative intermediates $[\{^tBuMe_2SiC_5H_4\}Co(NO)_2]$ and $[Tp^*Co(NO)_2]$ generated at −78 °C from **2** was observed. Reported in Table 5, *tris*(pyrazolyl) borate and cyclopentadienyl dinitrosoalkane complexes of strained alkenes and non-enolizable alkenes could be isolated in modest yields (**4k**–**r**, Table 5). Reactions were conducted at initial alkene concentrations of 0.1–0.5 M. The substrate scope and reaction selectivity follows trends previously established for reactions of alkenes with $[CpCo(\mu{-}NO)]_2$/NO mixtures [17–19]. While for bicyclo[2.2.1]alkenes addition of the $[\{L_2X\}Co(NO)_2]$ fragment occurs in exclusively an *exocyclic* fashion, for bicyclo[2.2.2]alkenes it may be expected that a mixture of isomers would result due to poorer control of facial selectivity in the addition step. Indeed, the reaction of **2**, NaCp and 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene yields an approximate 1:1 mixture of *endo*-**4q** and *exo*-**4q**. Readily separable by chromatography the connectivity of these isomers was assigned based on a single crystal X–ray diffraction experiment on *endo*-**4q**. The low quality of the collected data prevents a detailed discussion, but the stereochemistry of the product was determined unambiguously (see Figure S2).

In the absence of an alkene trap the five coordinate dinitrosyl cobalt complexes $[CpCo(NO)_2]$ and $[Tp^*Co(NO)_2]$ readily undergo dissociation of a single NO ligand. While we are reporting elsewhere that the paramagnetic complex $[Tp^*Co(NO)]$ may be synthesized from **2** and KTp* [20], the reversible addition of nitric oxide to $[CpCo(\mu{-}NO)]_2$ has been documented [17,18]. In the latter case it appears that the limited steric profile of the cyclopentadienyl ligand results in dimerization of the transient 17-electron intermediate [CpCoNO]. The reversibility of this reaction was further evidenced by performing the reaction of **2** with $[Li\{^tBuMe_2SiC_5H_4\}]$ in the absence of an alkene trap. Performing the latter reaction, $[\{^tBuMe_2SiC_5H_4\}Co(\mu{-}NO)]_2$ was isolable as a pale green solid in moderate yield following chromatography on silica gel under an inert glovebox atmosphere.

4. Summary and conclusions

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 reaction with alkenes, is reported. In support of existing precedent, four coordinate complexes are thermally robust and readily isolable species while five coordinate complexes are thermally unstable transient intermediates that readily undergo dissociation of an NO ligand. These latter complexes may be trapped by alkenes to form the corresponding metal dinitrosoalkane complexes. We are continuing to study the chemistry of dinitrosyl complexes of the late transition metals.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.04.038.

References

[1] (a) G.B. Richter-Addo, P. Legzdins, Metal Nitrosyls. Oxford University Press, New York, 1992, 233–270;
(b) C.A. Bosworth, J.C. Toledo Jr., J.W. Zmijewski, Q. Li, J.R. Lancaster Jr., Proc. Natl. Acad. Sci. U.S.A. 106 (2009) 4671;
(c) A.F. Vanin, Nitric Oxide 21 (2009) 1;
(d) Z.J. Tonzetich, L.E. McQuade, S.J. Lippard, Inorg. Chem. 49 (2010) 6338.

[2] (a) Y.-K. Chen, W.-C. Ku, L.-T. Feng, M.-L. Tsai, C.-H. Hsieh, W.-H. Hsu, W.-H. Liaw, C.-H. Hung, Y.-J. Chen, J. Am. Chem. Soc. 130 (2008) 10929;
(b) F.T. Tsai, P.-L. Chen, W.F. Liaw, J. Am. Chem. Soc. 132 (2010) 5290;
(C) C.H. Hsieh, M.Y. Darensbourg, J. Am. Chem. Soc. 132 (2010) 14118.

[3] (a) T.C. Harrop, D. Song, S.J. Lippard, J. Am. Chem. Soc. 128 (2006) 3528;
(b) T.C. Harrop, Z.J. Tonzetich, E. Reisner, S.J. Lippard, J. Am. Chem. Soc. 130 (2008) 15602;
(c) Z.J. Tonzetich, L.H. Do, S.J. Lippard, J. Am. Chem. Soc. 131 (2009) 7964;
(d) E. Tinberg, Z.J. Tonzetich, H. Wang, L.H. Do, Y. Yoda, S.P. Cramer, S.J. Lippard, J. Am. Chem. Soc. 132 (2010) 18168.

[4] (a) B. Haymore, R.D. Feltham, Inorg. Synth. 14 (1973) 81;
(b) A.G. Tennyson, S. Dhar, S.J. Lippard, J. Am. Chem. Soc. 130 (2008) 15087;
(c) Z.J. Tonzeyich, F. Heroguel, L.H. Do, Lippard S. J. Inorg. Chem. 50 (2011) 1570.

[5] J.H. Enemark, R.D. Feltham, Coord. Chem. Rev. (1974) 13.

[6] L.F. Dahl, E. Rodulfo de Gil, R.D. Feltham, J. Am. Chem. Soc. 91 (1969) 1653.

[7] (a) D.G. Gwost, K.G. Caulton, Inorg. Chem. 12 (1973) 2095;
(b) D.G. Gwost, K.G. Caulton, Inorg. Synth. 16 (1976) 16;
(c) V.W. Hieber, K. Kaiser, Z. Anorg. Allg. Chem. 362 (1968) 169;
(d) A.D. Zotto, A. Mezzetti, P. Rigo, Inorg. Chim. Acta 171 (1990) 61;
(e) T. Bianco, M. Rossi, L. Uva, Inorg. Chim. Acta 3 (1969) 443;
(f) W. Hieber, K. Heinicke, Z. Anorg. Allg. Chem. 316 (1962) 305.

[8] (a) B.E. Reichert, Acta Cryst. B32 (1976) 1934;
(b) A.M.M. Lanfredi, A. Tiripicchio, M.T. Camellini, Acta Cryst. C39 (1983) 1633;
(c) J.L. Roustan, N. Ansari, Y.L. Page, J.-P. Charland, Can. J. Chem. 70 (1992) 1650;
(d) J.A. Kaduk, J.A. Ibers, Inorg. Chem. 16 (1977) 3283.

[9] R. Seeber, G. Albertin, G.A. Mazzocchin, J. Chem. Soc. Dalton Trans. (1982) 2561.

[10] (a) D. Ballivet, I. Tkatchenko, J. Mol. Cat. 1 (1976) 319;
(b) D. Ballivet, I. Tkatchenko, Inorg. Chem. 16 (1977) 945.

[11] V.W. Hieber, H. Fuehrling, Z. Anorg. Allg. Chem. 377 (1970) 29.

[12] (a) A.R. Hendrickson, R.K.Y. Ho, R.L. Martin, Inorg. Chem. 13 (1974) 1279;
(b) R.L. Martin, D. Taylor, Inorg. Chem. 15 (1976) 2970.

[13] (a) J.K. Franz, N. Singh, B. Spingler, S.J. Lippard, Inorg. Chem. 39 (2000) 4081;
(b) S.A. Hiderbrand, S.J. Lippard, Inorg. Chem. 43 (2004) 4674.

[14] M. Aresta, D.B. Tkatchenko, M.C. Bonnet, R. Faure, H. Loisseleur, J. Am. Chem. Soc. 107 (1985) 2994.

[15] (a) J.S. Field, P.J. Wheatley, J. Chem. Soc. Dalton Trans. (1974) 74;
(b) B.L. Haymore, J.C. Huffman, N.E. Butler, Inorg. Chem. 22 (1983) 168.

[16] W. Hieber, H. Fuehrling, Z. Anorg. Allg. Chem. 373 (1970) 48.

[17] (a) H. Brunner, S. Loskot, Angew. Chem. Int. Ed. 10 (1971) 515;
(b) H. Brunner, S. Loskot, J. Organomet. Chem. 61 (1973) 401;
(c) G. Evrard, R. Thomas, B.R. Davis, I. Bernal, J. Organomet. Chem. 124 (1977) 59.

[18] (a) P.N. Becker, M.A. White, R.G. Bergman, J. Am. Chem. Soc. 102 (1980) 5676;
(b) P.N. Becker, R.G. Bergman, Organometallics 2 (1983) 787;
(c) P.N. Becker, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 2985.

[19] (a) J.M. Schomaker, W.C. Boyd, I.C. Stewart, F.D. Toste, R.G. Bergman, J. Am. Chem. Soc. 130 (2008) 3777;
(b) J.M. Schomaker, F.D. Toste, R.G. Bergman, Org. Lett. 11 (2009) 3698;
(c) W.C. Boyd, M.R. Crimmin, L.E. Rosebrugh, J.M. Schomaker, F.D. Toste, R.G. Bergman, J. Am. Chem. Soc. 132 (2010) 16365.

[20] N.C. Tomson, M.R. Crimmin, T. Petrenko, L.E. Rosebrugh, S. Sproules, W.C. Boyd, R.G. Bergman, S. DeBeer, F.D. Toste, K. Wieghardt, Manuscript in preparation.

[21] J.P.N. Brewer, I.F. Eckhard, H. Heaney, B.A. Marples, J. Chem. Soc. C (1968) 664.

[22] Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, P.P. Power, Organometallics 20 (2001) 1190.

[23] (a) P. Jutzi, R. Sauer, J. Organomet. Chem. 50 (1973) C29;
(b) A. Razavi, J.L. Atwood, J. Organomet. Chem. 459 (1993) 117;
(c) M.A. Edelman, P.B. Hitchcock, M.F. Lappert, D.-S. Liu, S. Tian, J. Organomet. Chem. 550 (1998) 397;
(d) M.F. Sullivan, W.F. Little, J. Organomet. Chem. 8 (1967) 277.

[24] (a) L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837–838;
(b) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; Göttingen, 1997.

[25] In regards to the definition of tris(pyrazolyl)borates as L2X type ligands, we defer to Crabtree, R. H. The Organometallic Chemistry of the Transition Metals, fifth ed. Wiley, 2009, 143

[26] (a) D.T. Shay, G.P.A. Yap, L.N. Zakharov, A.K. Rheingold, K.H. Theopold, Angew. Chem. Int. Ed. 44 (2005) 1508;
(b) S. Thyagarajan, D.T. Shay, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 125 (2003) 4440;
(c) J.D. Jewson, L.M. Liable-Sands, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Organometallics 18 (1999) 300;
(d) J.L. Detrich, R. Konecny, W.M. Vetter, D. Doren, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 118 (1996) 1703;
(e) O.M. Reinaud, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Angew. Chem. Int. Ed. 34 (1995) 2051;
(f) O.M. Reinaud, K.H. Theopold, J. Am. Chem. Soc. 116 (1994) 6979.

[27] S. Thyagarajan, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, Inorg. Chim. Acta 345 (2003) 333.

[28] J.L. Detrich, O.M. Reinaud, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 117 (1995) 11745.

[29] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349.