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Tetramethylcyclobutadienecobalt(I) complexes containing pyrazolate or tetrazolate ligands with various coordination modes

Oussama M. El-Kadri [1], Mary Jane Heeg, Charles H. Winter*

Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202, USA

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ABSTRACT

Treatment of $Cb^{*}Co(CO)_2I$ ($Cb^{*} = \eta^4$-C_4Me_4) with one equivalent of potassium 3,5-dimethylpyrazolate (Me_2pzK) or potassium 3,5-bis(trifluoromethyl)pyrazolate ($(CF_3)_2pzK$) in tetrahydrofuran at 0 °C afforded (η^4-$C_4Me_4(Me_2pz))Co(CO)_2$ and $Cb^{*}Co((CF_3)_2pz)(CO)_2$ in 90 and 71% yields, respectively. Treatment of $Cb^{*}Co(CO)_2I$ with one equivalent of Me_2pzH followed by the addition of one equivalent Me_2pzK in tetrahydrofuran afforded $Cb^{*}Co(Me_2pzH)(Me_2pz)(CO)$ in 74% yield. The reaction of $Cb^{*}Co(CO)_2I$ with one equivalent of potassium phenyl tetrazolate (PhtetzK) in tetrahydrofuran at 0 °C afforded $[Cb^{*}Co(Phtetz)(CO)]_2$ in 44% yield. The solid state structure of (η^4-$C_4Me_4(Me_2pz))Co(CO)_2$ revealed nucleophilic addition of a pyrazolate nitrogen atom to a Cb^{*} ligand carbon atom to afford a novel tetradentate ligand that bonds to the cobalt ion through an η^3-π-allyl interaction and one pyrazolyl nitrogen atom. Two carbonyl ligands are also present. An X-ray crystal structure determination of $Cb^{*}Co((CF_3)_2pz)(CO)_2$ showed η^1-coordination of the $(CF_3)_2pz$ ligand and η^4-coordination of the Cb^{*} ligand. The solid state structure of $Cb^{*}Co(Me_2pz)(Me_2pzH)(CO)$ is monomeric with one η^1-Me_2pz, one η^1-Me_2pzH, two carbonyl, and one η^4-Cb^{*} ligands. The η^1-Me_2pz and η^1-Me_2pzH ligands are linked by a hydrogen bond involving the uncoordinated nitrogen atoms. The X-ray crystal structure determination of $[Cb^{*}Co(Phtetz)(CO)]_2$ showed a dimeric molecular structure with two μ:η^1,η^1-Phtetz ligands connected to the cobalt ions through the 2- and 3-nitrogen atoms, one η^4-Cb^{*} ligand, and one carbonyl ligand per cobalt center. (η^4-$C_4Me_4(Me_2pz))Co(CO)_2$ is highly volatile and sublimes at 60 °C/0.03 Torr.

1. Introduction

The chemistry of complexes containing the CbCo (Cb = η^4-C_4H_4) fragment and ring substituted analogs has not been as widely explored as that of complexes containing CpFe fragments, in spite of their close chemical resemblance [1,2]. A major obstacle to the development of CbCo chemistry has been the lack of suitable starting materials. Tetraaryl-substituted CbCo complexes were prepared by treatment of $Co_2(CO)_8$ with $[(C_4Ar_4)Pd(CO)_2X]_2$ (Ar = Ph, p-tolyl; X = Cl, Br, I) [3], but require a stoichiometric palladium reagent. Alkyne dimerization at the cobalt centers of CpCo complexes leads to numerous CpCoCb derivatives, including those containing aryl substituents attached to the cyclobutadiene core [4].

Reports by Pauson et al. [5] and Kudinov et al. [6] described simple synthetic procedures for the preparation of $Cb^{*}Co(CO)_2I$ ($Cb^{*} = C_4Me_4$) in high yields. The availability of $Cb^{*}Co(CO)_2I$ has allowed broad access to $Cb^{*}Co$-containing complexes [5–7]. The methyl groups on the Cb^{*} ligand make it similar sterically to the Cp^{*} ligand. The Cp^{*} ligand has found many applications in stabilizing metal complexes across the periodic table, due to its strong electron donating character and steric profile imparted by the methyl groups [8].

A research goal in our laboratory is to develop volatile, thermally stable, and reactive cobalt source compounds for the growth of cobalt-containing thin films by atomic layer deposition (ALD). Cobalt-based thin films are of particular interest for use in microelectronics, magnetic information storage, gas sensors, and catalysis [9]. ALD requires precursors that are volatile, thermally stable at the film growth temperature, and which are highly reactive toward a second reagent to afford the desired thin film material [10]. We have previously established that pyrazole-derived metal complexes possess enhanced thermal stability, relative to complexes containing many other classes of ligands, and can lead to precursors that are useful in ALD [11]. We

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* Corresponding author. Tel.: +1 (313) 577 5224; fax: +1 (313) 577 8289.
E-mail address: chw@chem.wayne.edu (C.H. Winter).

[1] Present address: Department of Biology and Chemistry, American University of Sharjah, P.O. Box 26666, Sharjah, United Arab Emirates.

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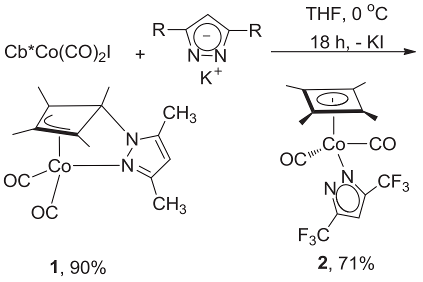
therefore sought to prepare cobalt complexes containing pyrazolate ligands to assess their suitability for use as ALD precursors. Herein, we describe the synthesis and characterization of cobalt(I) complexes containing the Cb*Co(CO)$_x$ ($x = 1$ or 2) fragments along with a various pyrazolate-derived ligands. A complex containing a tetrazolate ligand is also described. A surprising result from this study is nucleophilic attack on the Cb* ligand by the Me_2pz fragment. The volatility and thermal stability of the new complexes are also reported.

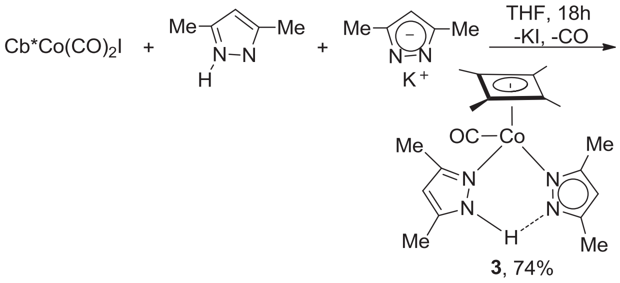
2. Results and discussion

Treatment of Cb*Co(CO)$_2$I [6] with one equivalent of Me_2pzK or $(CF_3)_2pzK$ in tetrahydrofuran at 0 °C, followed by stirring at room temperature for 18 h, afforded (η^4-C_4Me_4(Me_2pz))Co(CO)$_2$ (**1**, 90%) and Cb*Co((CF_3)$_2$pz)(CO)$_2$ (**2**, 71%) as yellow microcrystalline solids after workup (eq (1)). The formulations and molecular structures of **1** and **2** were established by a combination of spectral and analytical data, as well as by X-ray crystal structure determinations. The solid state structure of **1** revealed nucleophilic addition of a pyrazolate nitrogen atom to the Cb* ligand to afford a novel tetradentate ligand that bonds to the cobalt ion through a η^3-π-allyl interaction and one pyrazolyl nitrogen atom. Two carbonyl ligands are also present. By contrast, **2** contains one η^4-Cb*, one η^1-(CF_3)$_2$pz, and two carbonyl ligands. The ^{1}H NMR spectra of **1** and **2** are uniquely consistent with the solid-state structures. At 21 °C in benzene-d_6, the ^{1}H NMR spectrum of **1** consisted of a sharp singlet at δ 5.35 for the pyrazolyl moiety ring hydrogen atom, and two sharp singlets at δ 1.82 and 1.65 for the pyrazolyl methyl groups. In addition, three singlets were observed at δ 2.17, 1.36, and 1.06 in a 1:2:1 ratio, respectively, for the chemically unique methyl groups of the η^3-Cb*-derived fragment.



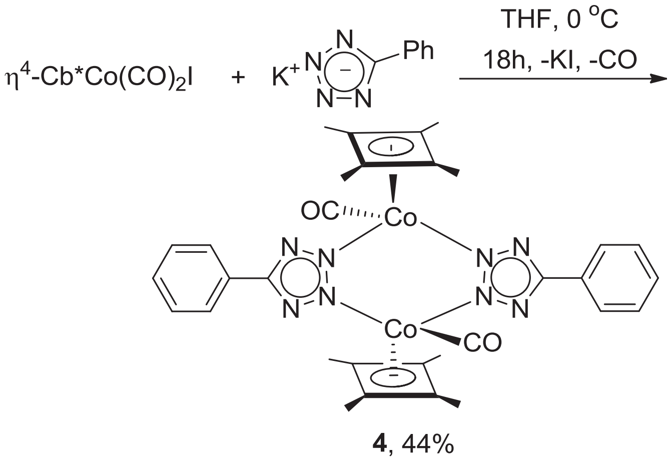
(1)

In several syntheses of **1**, an additional product was isolated, which appeared to have the formula Cb*Co(Me_2pz)(Me_2pzH)(CO) (**3**) from ^{1}H NMR analysis. To assess this possibility, Cb*Co(CO)$_2$I was treated with an equimolar quantity of Me_2pzH in tetrahydrofuran, followed by one equivalent Me_2pzK, to afford **3** in 74% yield as red crystals after workup (eq (2)). Complex **3** is monomeric in the solid state with one η^4-Cb*, one η^1-Me_2pz, one η^1-Me_2pzH, and one carbonyl ligands. The η^1-Me_2pz and η^1-Me_2pzH ligands are linked by a hydrogen bond between the uncoordinated nitrogen atoms. The ^{1}H NMR spectrum of **3** at 21 °C in benzene-d_6 solution consisted of a sharp singlet at δ 5.86 for the η^1-Me_2pz and η^1-Me_2pzH ring hydrogen atoms, two singlets at δ 2.28 and 2.24 for the methyl groups of the η^1-Me_2pz and η^1-Me_2pzH ligands, the N–H resonance at δ 1.96, and a sharp singlet at δ 0.82 for the methyl groups of the Cb* ligands. Observation of a single ring hydrogen atom resonance and only two methyl group resonances for the η^1-Me_2pz and η^1-Me_2pzH ligands implies that proton transfer between these two ligands is rapid at 21 °C.



(2)

The dimeric phenyl tetrazolate complex [Cb*Co(Phtetz)(CO)]$_2$ (**4**) was prepared in 44% yield by treatment of Cb*Co(CO)$_2$I with one equivalent of the potassium 5-phenyl tetrazolate in tetrahydrofuran (eq (3)). The structural assignment for **4** was based upon spectral and analytical data, as well as an X-ray crystal structure determination. The X-ray crystal structure of **4** established a dimeric constitution with two μ:η^1,η^1-phenyl tetrazolate ligands connected to the cobalt ions through the 2- and 3-nitrogen atoms, as well as one η^4-Cb* and one carbonyl ligand per cobalt center. Interestingly, the ^{1}H NMR spectrum of **4** in toluene-d_8 reveals the presence of two isomers. In toluene-d_8, the ratio of these two isomers was invariant at about 70:30 between −40 and +80 °C. At −60 and −80 °C, the ratios changed slightly to 61:39 and 58:42, respectively. The origin of these isomers is not fully clear. In the solid state, **4** exists with *anti*-disposition of the carbonyl and Cb* ligands within the dimer. It is possible that the isomers correspond to complexes containing *anti*- and *syn*-dispositions of the carbonyl and Cb* ligands within the dimer.



(3)

The crystal structures of **1**–**4** were determined to establish the geometry about the metal centers and to assess the bonding modes of the ligands. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are presented in Tables 2–5, and perspective views are given in Figs. 1–4.

A perspective view of **1** is shown in Fig. 1. The Co–C bond distances associated with the η^3-C_4Me_4 fragment range from 2.002(1) to 2.061(1) Å, and the Co–N bond length is 2.027(9) Å. The C–N bond length formed by the nucleophilic attack of the pyrazolate nitrogen atom on the Cb* ligand is 1.477(1) Å. Complexes **2**–**4** share a common Cb*Co structural fragment (Figs. 2–4). The Cb* ligand in each of these complexes is coordinated to the Co ion through

Table 1
Crystal data and data collection parameters for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{15}H_{19}CoN_2O_2$	$C_{15}H_{13}CoF_6N_2O_2$	$C_{19}H_{27}CoN_4O$	$C_{32}H_{34}Co_2N_8O_2$
Fw	318.25	426.20	386.38	680.53
Space group	C2/c	P1	$P2_1/n$	$P2_1/c$
a (Å)	25.1187(7)	6.8415(2)	8.1635(3)	8.5631(2)
b (Å)	9.5441(3)	9.5852(3)	17.4908(5)	11.6664(3)
c (Å)	15.5266(4)	14.2602(5)	13.5892(3)	16.0505(4)
α (deg)		102.865(2)		
β (deg)	125.8960(10)	103.398(2)	94.0930(10)	93.0420(10)
γ (deg)		92.654(2)		
$V(Å^3)$	3015.35(15)	882.12(5)	1935.40(10)	1601.19(7)
Z	8	2	4	2
Temp (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ calcd (g cm^{-3})	1.402	1.605	1.326	1.412
μ (mm^{-1})	1.140	1.044	0.900	1.078
R(F)(%)	2.65	3.44	3.28	3.03
$R_w(F^2)$(%)	6.62	7.46	8.05	7.61

$R(F) = \sum\|Fo\| - \|Fc\|/\sum\|Fo\|$; $Rw(F) = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

η^4-bonding, with Co–C bond lengths from 1.981(1) to 2.098(1) Å. The C–C bond lengths within the Cb* ligands vary from 1.424(10) to 1.554(2) Å. Complexes **1**–**4** also contain one or two carbonyl ligands, with Co–C bond distances ranging from 1.775(1) to 1.813(1) Å. The Co–N bond distance in **2** is 1.993(1) Å. In addition to the Cb* and carbonyl ligands, **3** contains η^1-Me_2pz and η^1-Me_2pzH ligands that are connected by a hydrogen bond between the uncoordinated nitrogen atoms. The Co–N bond lengths for the η^1-Me_2pz (Co–N(1)) and η^1-Me_2pzH (Co–N(3)) ligands are 2.010(1) and 2.029(9) Å, respectively. In **4**, a dimeric structure results through adoption of two μ:η^1,η^1-Phtetz ligands connected to the cobalt ions through the 2- and 3-nitrogen atoms. The dimer **4** occupies a crystallographic 2-fold axis that relates the two halves of the molecule. The Co–N bond lengths associated with the Phtetz ligands are 1.984(1) and 1.996(1) Å.

Many cobalt(I) complexes containing the Cb*Co fragment have been structurally characterized. A review gives a comprehensive list of Cb*Co complexes that also contain halide, cyclopentadienyl, hydrocarbon, and other anionic donor ligands [2c]. The metrical parameters associated with the Cb*Co(CO)$_x$ (x = 1 or 2) fragments in **1**–**4** are similar to those found in related Cb*Co(CO)$_x$ complexes (Co–C (Cb* carbon) ~1.97 Å, Co–C (carbonyl carbon) ~1.75 Å) [2c,6,7]. Complexes containing Cb*Co fragments generally form metallocene-like sandwich complexes cyclopentadienyl ligands. There was no evidence for the formation of η^5-pyrazolate complexes during the preparations of **1**–**4**, even though the pyrazolate ligand is similar electronically to cyclopentadienyl ligands and we have previously reported η^5-pyrazolate and η^5-imidazolate complexes of ruthenium(II) and osmium(II) [12]. It is likely that the Co–C bond energies of the carbonyl ligands are higher than the Co–C and Co–N bond energies that would be obtained upon formation of η^5-pyrazolate or η^5-tetrazolate ligands, and thus, only η^1-azolate ligand coordination is observed in **2**–**4** and a nucleophilic addition occurs instead in **1**.

Table 3
Selected bond lengths [Å] and angles [deg] for **2**.

Co–N(1)	1.993(1)
Co–C(6)	1.813(2)
Co–C(7)	1.808(2)
Co–C(8)	2.098(2)
Co–C(9)	2.029(2)
Co–C(10)	2.002(1)
Co–C(11)	2.066(2)
Co–N(1)–N(2)	115.38(9)
C(6)–Co–C(7)	101.34(7)
C(6)–Co–N(1)	95.71(6)
C(7)–Co–N(1)	104.47(6)

There are several previous reports of nucleophilic additions to transition metal cyclobutadiene complexes to form cyclobutenyl ligands. Maitlis described treatment of $[MCp(C_4Ph_4)]^+Br^-$ (M = Ni, Fe) with hydroxide or ethoxide ions to afford the products in which the oxygen nucleophiles added to the C_4Ph_4 ligands [13]. These products were not structurally characterized, but it was proposed that the nucleophilic additions occurred at the *exo*-face of the C_4Ph_4 ligands [13]. Addition of a range of nucleophiles to the cyclobutadiene ligand in $[Fe(C_4H_4)(CO)_2NO]^+$ occurs exclusively at the *exo*-face, and several products were structurally characterized [14]. Treatment of Cb*$NiCl_2$ with two equivalents of C_5H_5Na affords CpNi(η^3-$C_4Me_4(C_5H_5)$) [15], and an X-ray crystal structure demonstrated that the C_5H_5 group is situated on the *exo*-face of the C_4Me_4 group. The complex 5,7,8-Me_3-11,7,8,10-[η^3-C_4Me_4H]$NiC_3B_7H_7$ was obtained upon treatment of nickel atoms with 2,6-$C_2B_7H_{11}$ and 2-butyne [16]. The solid state structure reveals an η^3-C_4Me_4H ligand with the ring-bound hydrogen atom residing on the *exo*-face. X-ray crystal structures were reported for the *exo*- and *endo*- isomers of $Pd_2Cl_2(\eta^3$-$C_4Ph_4OEt)_2$, which were obtained upon treatment of $PdCl_2$ with diphenylacetylene in ethanol [17]. CpNi(η^3-$C_4Me_4(C_5H_5)$), 5,7,8-Me_3-11,7,8,10-[η^3-C_4Me_4H]$NiC_3B_7H_7$, and $Pd_2Cl_2(\eta^3$-$C_4Ph_4OEt)_2$ are likely formed by nucleophilic attack of $C_5H_5^-$, hydride, and ethoxide, respectively, upon intermediate cyclobutadiene species. The complex Co(η^4-$C_4(CF_3)_4(Et_2PS)$)(CO)(PPh_3) contains an η^3-cyclobutenyl ligand in which there is a C–P bond between the uncoordinated cyclobutenyl core C atom and the P atom of the Et_2PS fragment, as well as a Co–S bond [18]. Such a configuration resembles the *endo*-disposition of the Me_2pz fragment in **1**. However, Co(η^4-$C_4(CF_3)_4(Et_2PS)$)(CO)(PPh_3) was formed by treatment of Co(η^2-Et_2PS)$(CO)_2PPh_3$ with hexafluoro-2-butyne and did not entail a nucleophilic attack upon a cyclobutadiene ligand. The formation of Co(C_5H_5)(η^4-tetraethyl-α-pyrone) upon treatment of Co(η^4-C_4Et_4)$(CO)_2I$ with $C_5H_5^-$ and ethyl formate was proposed to proceed through an intermediate resulting from nucleophilic attack of a cyclobutadiene

Table 2
Selected bond lengths [Å] and angles [deg] for **1**.

Co–N(1)	2.027(1)
Co–C(1)	1.773(1)
Co–C(2)	1.767(1)
Co–C(9)	2.042(1)
Co–C(10)	2.002(1)
Co–C(11)	2.061(1)
N(2)–C(8)	1.477(1)
Co–N(1)–C(1)	106.85(7)
C(1)–Co–C(2)	97.67(5)
C(1)–Co–N(1)	110.13(4)
C(2)–Co–N(1)	114.38(5)

Table 4
Selected bond lengths [Å] and angles [deg] for **3**.

Co–N(1)	2.010(1)
Co–N(3)	2.029(1)
Co–C(11)	2.043(1)
Co–C(12)	1.985(1)
Co–C(13)	2.028(1)
Co–C(14)	2.094(1)
Co–C(19)	1.775(1)
Co–N(1)–N(2)	118.61(6)
Co–N(3)–N(4)	117.98(7)
N(1)–Co–N(3)	93.29(3)
N(1)–Co–C(19)	104.39(4)
N(3)–Co–C(19)	99.86(4)

Table 5
Selected bond lengths [Å] and angles [deg] for **4**.

Co–N(1)	1.984(1)
Co′–N(4)	1.996(1)
Co–C(1)	1.993(1)
Co–C(2)	1.981(1)
Co–C(3)	2.097(1)
Co–C(4)	2.098(1)
Co–C(16)	1.783(1)
Co–N(1)–N(4)	129.91(8)
N(1)–Co–N(4)′	98.58(4)
N(1)–Co–C(16)	97.76(5)
N(4)′–Co–C(16)	100.47(5)

carbon atom on the ethyl formate carbonyl group [19]. The resulting proposed intermediate contains an η^4-cyclobutenyl ligand that is bonded to cobalt through three of the cyclobutenyl carbon atoms and through the resultant alkoxy-like oxygen atom. This proposed η^4-cyclobutenyl ligand has a chelating structure similar to that of **1**. Treatment of Fe(η^4-C_4R_4)(CO)$_3$ (R = H, Me) with tetrafluoroethylene, hexafluofluoropropene, or hexafluoroacetone led to products in which the unsaturated bonds inserted into an iron-carbon bond of the η^4-C_4R_4 ligand to afford complexes containing η^4-cyclobutenyl ligands with chelating structures similar to that of **1** [20].

In the present study, the pyrazolate moiety in **1** is bonded to the *endo*-face of the C_4Me_4 fragment, suggesting that the Me_2pz ion first displaces the iodide ion in Cb*Co(CO)$_2$I to form intermediate Cb*Co(CO)$_2$(Me$_2$pz), which then undergoes intramolecular *endo*-nucleophilic addition to afford **1**. More complex reaction mechanisms are also possible that could entail nuclophilic attack on the *exo*-face of the Cb* ligand, followed by isomerization of the π-allyl fragment to form **1**. While *exo*-attack cannot be ruled out, the proposed *endo*-attack is simpler in that it does not require an isomerization step. The structure of **2** represents an interesting comparison with that of **1**. In **2**, the η^1-(CF$_3$)$_2$pz ligand has not undergone nucleophilic addition to the Cb* ligand, presumably due to the lower basicity of the nitrogen atoms arising from the electron withdrawing trifluoromethyl groups and the greater ability of the (CF$_3$)$_2$pz ligand to stabilize a negative charge, compared to a π-allyl fragment.

To assess their initial viability as ALD precursors, sublimation studies were carried out on **1**–**3**. In preparative sublimations (~0.5 g), **1** sublimed at 60 °C/0.03 Torr over 5 h to afford unchanged **1** in 83% recovered yield. There was a 4% nonvolatile residue at the completion of the sublimation. The ^1H and $^{13}C\{^1H\}$ NMR spectrum of sublimed **1** were identical to the material before sublimation, demonstrating that no reaction occurred during the sublimation process. Complexes **2** and **3** did not sublime below 200 °C at 0.03 Torr, and instead decomposed to black, insoluble, nonvolatile materials. Sublimation studies of **4** were not conducted, due to the dimeric structure, the high nitrogen content, and attendant risk of detonation. The thermal stability of **1** was further studied by measuring its melting point and solid state decomposition temperature. Complex **1** melts from 112 to 114 °C and shows no color change at this temperature. Upon further heating, **1** changes color from orange to black at 136–138 °C, indicating decomposition. The 4% residue observed upon sublimation of **1** and the low decomposition temperature suggest that **1** does not have enough thermal stability to serve as an ALD precursor [10]. However, its low sublimation temperature may allow use of **1** in CVD film growth procedures, where precursor thermal stability requirements are not as strict.

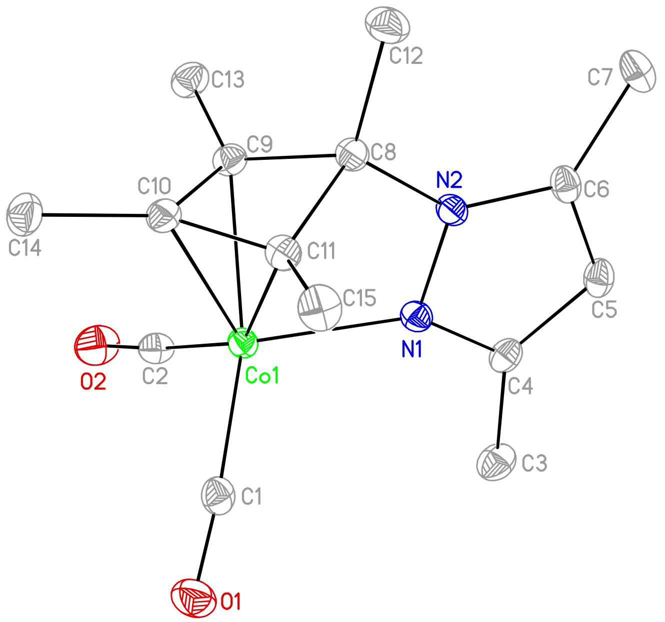


Fig. 1. Perspective view of **1** with thermal ellipsoids at the 50% probability level.

3. Experimental

3.1. General considerations

All reactions were carried out under argon using either glovebox or Schlenk line techniques. Toluene was distilled from sodium, tetrahydrofuran was distilled from sodium benzophenone ketyl, and hexane was distilled from P_2O_5. Cb*Co(CO)$_2$I [6] and Me$_2$pzK [21] were prepared by literature procedures. Me$_2$pzH, (CF$_3$)$_2$pzH, and PhtetzH were purchased from Aldrich Chemical Company and were used as received.

^1H, $^{13}C\{^1H\}$, and ^{19}F NMR were obtained in benzene-d_6 or toluene-d_8 using 500, 400, or 300 MHz spectrometers. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana, USA. Melting points were obtained with a Haake-Buchler HBI digital melting point apparatus and are uncorrected. Preparative sublimations of **1**–**3** and solid state decomposition studies of **1** were performed according to previously described procedures [11b].

3.2. Preparation of (η^4-C_4Me_4(Me$_2$pz))Co(CO)$_2$ (**1**)

A 100-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, was charged with Cb*CoI(CO)$_2$ (0.501 g, 1.42 mmol) and tetrahydrofuran (20 mL) and was cooled to −78 °C. To this solution was added Me$_2$pzK (0.191 g, 1.44 mmol) that was dissolved in tetrahydrofuran (20 mL). The resultant orange solution was allowed to warm to room temperature and was stirred for 18 h. The solvent was then removed under reduced pressure to yield a yellow crystalline solid. This solid was extracted with hexane (40 mL) and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. Removal of the solvent under reduced pressure afforded **1** as a yellow crystalline solid (0.410 g, 90%): m.p. 114–116 °C; IR (Nujol, cm^{-1}) 1976 (ν_{CO}, s), 1911 (ν_{CO}, s); ^1H NMR (benzene-d_6, 21 °C, δ) 5.35 (s, 1H, pz ring C*H*), 2.17 (s, 3H, C*H*$_3$ of η^3-C_4Me_4), 1.82 (s, 3H, pz C*H*$_3$), 1.65 (s, 3H, pz C*H*$_3$), 1.34 (s, 6H, 2C*H*$_3$ of η^3-C_4Me_4), 1.06 (s, 3H, C*H*$_3$ of η^3-C_4Me_4); $^{13}C\{^1H\}$ (benzene-d_6, 21 °C, ppm) 207.24 (s, CO), 149.82 (s, pz *C*–CH$_3$), 137.72 (s, pz *C*–CH$_3$), 106.98 (s, pz ring *C*H), 102.99 (s, carbon atom on the C_4 ring that is connected to the pz ligand), 103.00 (s, *C*–N of η^3-C_4Me_4), 89.67 (s, 2*C*–CH$_3$ of η^3-C_4Me_4), 75.33 (s, *C*–CH$_3$ of η^3-C_4Me_4), 19.89 (s, *C*H$_3$), 14.22 (s, *C*H$_3$), 14.15 (s, *C*H$_3$), 11.92 (s, *C*H$_3$), 10.80 (s, 2*C*H$_3$ of η^3-C_4Me_4).

Anal. Calcd for $C_{15}H_{19}CoN_2O_2$: C, 56.61; H, 6.02; N, 8.80. Found: C, 56.76; H, 6.08; N, 8.92.

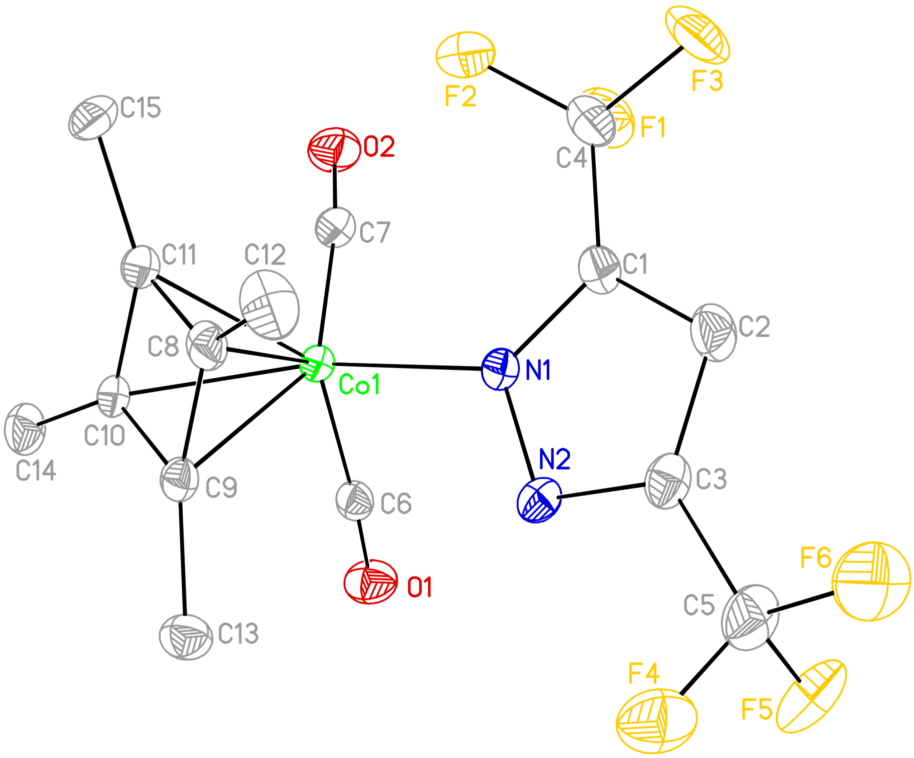


Fig. 2. Perspective view of **2** with thermal ellipsoids at the 50% probability level.

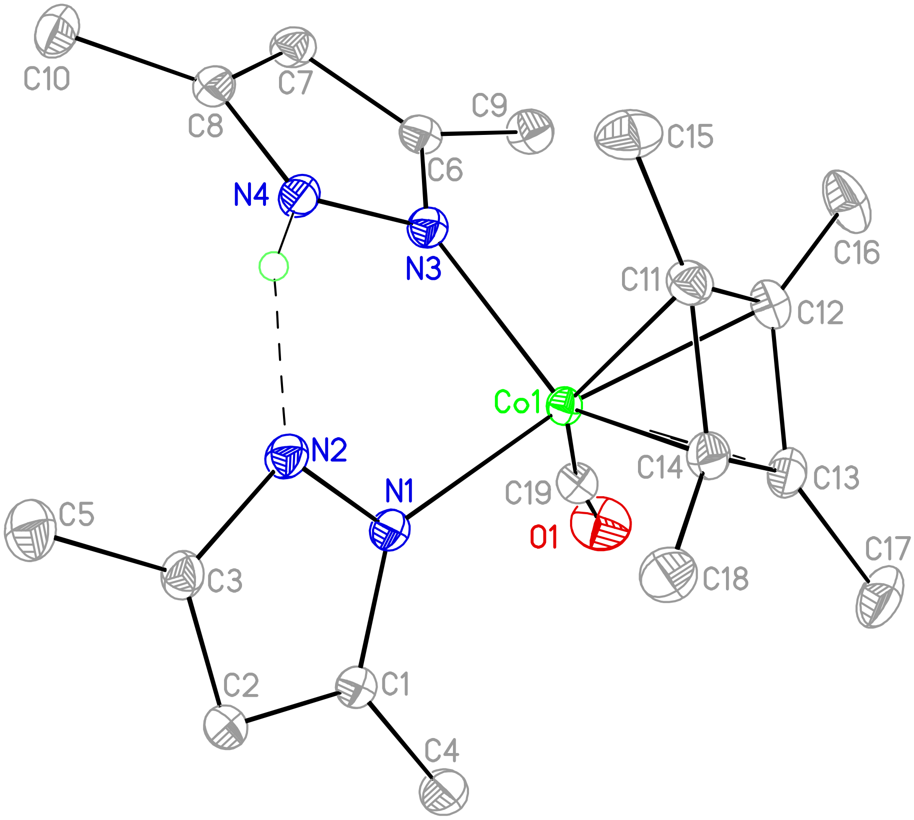


Fig. 3. Perspective view of **3** with thermal ellipsoids at the 50% probability level.

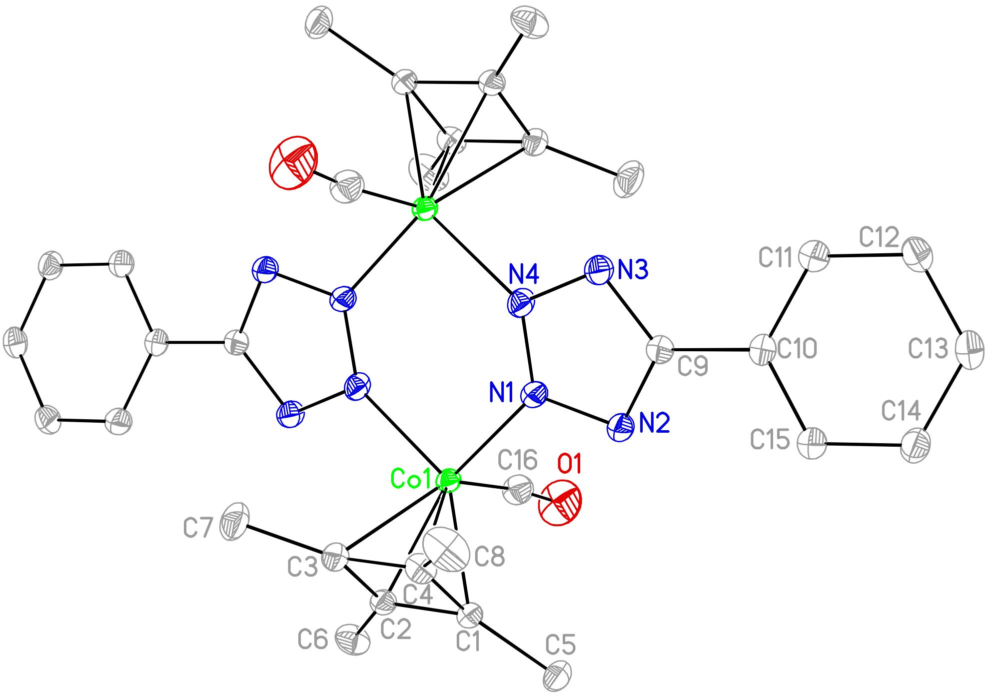


Fig. 4. Perspective view of **4** with thermal ellipsoids at the 50% probability level.

3.3. *Preparation of Cb*Co((CF$_3$)$_2$pz)(CO)$_2$ (**2**)*

In a fashion similar to the preparation of **1**, treatment of Cb*Co(CO)$_2$I (0.508 g, 1.45 mmol) with (CF$_3$)$_2$pzK (0.360 g, 1.49 mmol) afforded **2** as a yellow crystalline solid (0.431 g, 71%): m.p. 73–75 °C; IR (Nujol, cm^{-1}) 2053(ν_{CO}, s), 2016 (ν_{CO}, s); ^{1}H NMR (benzene-d_6, 21 °C, δ) 6.87 (s, 1H, pz *C*H), 0.78 (s, 12H, Cb* *C*H$_3$); ^{13}C{^{1}H} (benzene-d_6, 22 °C, ppm) 202.35 (s, *C*O), 145.20 (q, $J_{CCF} = 36$ Hz, *C*–CF$_3$), 142.99 (q, $J_{CCF} = 35$ Hz, *C*–CF$_3$), 123.12 (q, $J_{CF} = 266$ Hz, CF$_3$), 122.52 (q, $J_{CF} = 266$ Hz, CF$_3$), 106.08 (s, pz *C*H), 95.05 (s, Cb* *C*–CH$_3$), 8.08 (s, Cb* *C*H$_3$); ^{19}F NMR (benzene-d_6, 21 °C, δ) 123.58 (s, CF$_3$), 120.91 (s, CF$_3'$).

Anal. Calcd for $C_{15}H_{13}CoF_6N_2O_2$: C, 42.27; H, 3.07; N, 6.57. Found: C, 41.98; H, 3.17; N, 6.34.

3.4. *Preparation of Cb*Co(Me$_2$pz)(Me$_2$pzH)(CO) (**3**)*

A 100-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, was charged with Cb*Co(CO)$_2$I (0.310 g, 0.89 mmol), 3,5-dimethylpyrazole (0.845 g, 0.89 mmol), and tetrahydrofuran (20 mL). The resultant red solution was refluxed for 2 h and was then allowed to cool to room temperature. To this solution was added Me$_2$pzK (0.118 g, 0.89 mmol) that was dissolved in THF (20 mL). The resultant red solution was stirred at ambient temperature for 18 h. The solvent was then removed under reduced pressure to yield red crystalline solid. This solid was extracted with hexane (40 mL) and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. Removal of the solvent under reduced pressure afforded **3** as a afforded yellow crystalline solid (0.39 g, 84%): m.p. 148–150 °C; IR (Nujol, cm^{-1}) 3201 (w, ν_{NH}), 1952 (ν_{CO}, s); ^{1}H NMR (benzene-d_6, 21 °C, δ) 5.86 (s, 2H, pz and pzH *C*H), 2.28 (s, 6H, pz and pzH *C*H$_3$), 2.24 (s, 6H, pz and pzH *C*H$_3$), 1.96 (s, 1H, N–*H*), 0.82 (s, 12H, Cb* *C*H$_3$); ^{13}C{^{1}H} (benzene-d_6, 22 °C, ppm) 208.60 (s, *C*O), 151.16 (s, pz and pzH *C*CH$_3$), 144.84 (s, pz and pzH *C*CH$_3$), 105.53 (s, pz and pzH *C*H), 85.08 (s, Cb* *C*CH$_3$), 14.68 (s, pz and pzH *C*H$_3$), 12.39 (s, pz and pzH *C*H$_3$), 8.73 (s, Cb* *C*H$_3$).

Anal. Calcd for $C_{19}H_{27}CoN_4O$: C, 59.06; H, 7.04; N, 14.50. Found: C, 58.96; H, 6.92; N, 14.47.

3.5. *Preparation of [Cb*Co(Phtetz)(CO)]$_2$ (**4**)*

In a fashion similar to the preparation of **1**, treatment of Cb*Co(CO)$_2$I (0.351 g, 1.00 mmol) with potassium phenyl tetrazolate (PhtetzK) (0.186 g, 1.00 mmol) afforded **3** as red-colored crystals (0.151 g, 44%): m.p. 270–272 °C (dec); IR (Nujol, cm^{-1}) 1977 (ν_{CO}, s); ^{1}H NMR (benzene-d_6, 21 °C, δ) major isomer (78%): 8.45 (d, $J = 7.0$ Hz, 4H, o-C$_6$*H*$_2$H$'_2$H$''$), 7.27 (t, $J = 7.5$ Hz, m-C$_6$H$_2$*H*$'_2$H$''$), 7.15 (d, $J = 8.0$ Hz, p-C$_6$H$_2$H$'_2$*H*$''$), 1.01 (s, 12H, Cb* *C*H$_3$), minor isomer (22%): 8.44 (d, $J = 7.0$ Hz, 4H, o-C$_6$*H*$_2$H$'_2$H$''$), 7.18 (t, $J = 7.5$ Hz, m-C$_6$H$_2$*H*$'_2$H$''$), 7.16 (d, $J = 8.0$ Hz, p-C$_6$H$_2$H$'_2$*H*$''$), 1.09 (s, 12H, Cb* *C*H$_3$); ^{13}C{^{1}H} (benzene-d_6, 21 °C, ppm) major isomer only: 204.36 (s, *C*O), 166.95 (s, *C*–C$_6$H$_5$), 130.38 (s, ipso-*C* of Ph ring), 128.93 (s, ortho-*C*H of Ph ring), 128.18 (s, meta-*C*H of Ph ring), 126.57 (s, para-*C*H of Ph ring), 88.49 (s, Cb* *C*–CH$_3$), 8.94 (s, Cb* *C*CH$_3$).

Anal. Calcd for $C_{32}H_{34}Co_2N_8O_2$: C, 56.48; H, 5.04; N, 16.47. Found: C, 56.74; H, 5.15; N, 16.01.

3.6. *X-ray crystal structure determinations*

Diffraction data were measured on a Bruker X8 APEX-II kappa geometry diffractometer with Mo radiation and a graphite monochromator. Frames were collected at 100 K for 5–10 s/frame as a series of sweeps with the detector at 40 mm and 0.3° between each frame. APEX-II [22] and SHELX-97 [23] software were used in the collection and refinement of the models.

Crystals of **1** were obtained as yellow rods, and a sample measuring approximately 0.2 × 0.2 × 0.11 mm^3 was used for the data collection. 27187 reflections were integrated, of which 4858 were independent. Hydrogen positions were placed in observed positions and refined. The asymmetric unit contains one neutral molecule without solvent. Complex **2** crystallized as yellow rods and a crystal of dimensions 0.14 × 0.12 × 0.10 mm^3 was mounted and measured. 19827 reflections were integrated, yielding 5425 independent data. Hydrogen density was placed according to maps and refined. The asymmetric unit contains one neutral complex without solvent. Complex **3** formed red plates, and a cut fragment measuring 0.39 × 0.14 × 0.12 mm^3 was chosen for the diffraction experiment. 49433 spots were measured and averaged into 8316 independent reflections. Hydrogen atoms were placed in observed or calculated positions. The asymmetric unit contains one neutral molecule. Complex **4** crystallized as red rhomboids. The data crystal dimensions were 0.22 × 0.20 × 0.12 mm^3. 30942 data points were counted yielding 5321 independent observations. Hydrogen atoms were placed in observed or calculated positions. The complex exists as a dimer in the crystal and the asymmetric unit contains 1/2 of this dimer.

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Appendix A. Supplementary material

CCDC 789466–789469 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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