Isolation and Characterization of a Homoleptic Tetramethylcobalt(III) Distorted Square-Planar Complex

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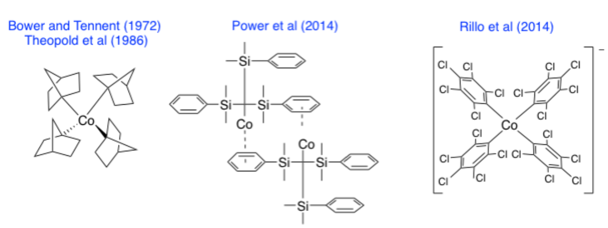
ABSTRACT: Homoleptic cobalt alkyl and aryl complexes are extremely rare, limited predominantly to complexes utilizing bulky, stabilizing ligands. There have been no reports to date of homoleptic cobalt species with simple, sterically unencumbered alkyl ligands, such as methyl. Herein, we report the synthesis and characterization of the homoleptic, distorted square planar tetramethylcobalt (III) complex $[Mg(acac)(NMP)_4][CoMe_4]$ (NMP = *N*-methylpyrrolidone), which exhibits extreme temperature and moisture sensitivities. NMR and density functional theory provide detailed insight into the electronic structure and bonding of this intermediate spin ($S = 1$) complex.

Cobalt alkyl complexes have been known since the 1960s, traditionally stabilized by ancillary ligands such as carbonyls or phosphines.[1-3] In the early 1970s, Bower and Tennent reported the first homoleptic alkylcobalt species, tetrakis(1-norbornyl)cobalt(IV), which has a tetrahedral geometry.[4-5] Since this initial study, there have been very few reports of homoleptic cobalt alkyl and aryl species, and those that exist rely on bulky ligands or ligands containing silyl groups, such as $[Co\{C(SiMe_2Ph)_3\}]_2$ (Scheme 1).[2] Even more rare are square planar homoleptic organocobalt(III) species. The only example of an organocobalt(III) square planar complex without sterically encumbered,[6] polydentate,[7-8] or heteroatom[9] containing ligands, and having Co-C bonds, was reported in 2014, where the tetraaryl complexes, $[Co(C_6X_5)_4]^-$ (X = F, Cl), were characterized by single crystal X-ray diffraction (SC-XRD) (Scheme 1).[10] Despite the growing field of organocobalt chemistry, there still lacks a fundamental understanding of cobalt speciation in the presence of simple alkyl Grignard reagents. These species could provide insight into the types of cobalt species accessible in various reactions, such as cobalt catalyzed cross-coupling reactions.[11-12] With recent success in our group in understanding the complex iron speciation in the presence of methylmagnesium bromide (MeMgBr)[13-15] and the recent report of homoleptic tetraarylcobalt species,[10] we were encouraged to explore cobalt speciation upon the introduction of cobalt salts to MeMgBr. Herein, we report the isolation and characterization of a homoleptic tetramethylcobalt(III) complex, $[CoMe_4]^-$ (**1**). NMR and density functional theory (DFT) studies show that this thermally unstable distorted square planar complex is an intermediate-spin ($S = 1$) system.



Scheme 1. Examples of previously reported homoleptic cobalt alkyl and aryl complexes.

Initial synthetic efforts focused on identifying the cobalt speciation of reactions of $Co(acac)_3$ (acac = acetylacetone) or $CoBr_2$ in THF in the presence of MeMgBr under conditions analogous to those of the previously reported $[FeMe_4]^-$ complex.[13] Unfortunately, there was no observation of crystalline material from these reactions. It was hypothesized the addition of *N*-methylpyrrolidone (NMP) would serve as a ligand to the magnesium counterion, allowing for the stabilization and isolation of a cobalt-methyl complex.[15-17] Upon the addition of excess MeMgBr (5 equiv, 1.0 M in THF) to a mixture of $Co(acac)_3$ and excess NMP (30 equiv) in Et_2O at -80 °C, red crystalline blocks formed, which were identified by SC-XRD as $[Mg(acac)(NMP)_4][CoMe_4]$ (**1**) (Figure 1). Unfortunately, due to the similar solubilities of the byproduct crystalline magnesium salts, an accurate percent yield of **1** could not be determined.

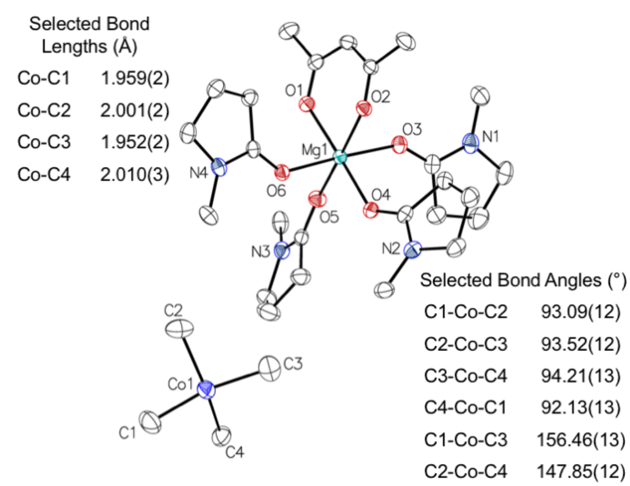


Figure 1. The crystal structure and selected bond distances and angles of $[Mg(acac)(NMP)_4][CoMe_4]$ drawn at 50% probability density with hydrogen atoms omitted for clarity. Only the major component of the methyl ligand disorder is depicted (see text and SI).

One methyl ligand (C4) is modeled as disordered over two positions (0.73:0.27). The refined Co1-C4 bond lengths for the two methyl positions were restrained to be similar. An independent structure containing a $[CoMe_4]^-$ anion, formulated as $[Mg(acac)(NMP)_4]_2[CoMe_4][Br] \cdot 2NMP$, is included in the SI. The latter structure also has a disordered methyl ligand, and because the $[CoMe_4]^-$ anion lies on a crystallographic inversion center, the disorder is propagated across the center. Therefore, all discussion of structural metrics below will be restricted to the major component of disorder of **1**.

The solid state structure of **1** is best described as a distorted square planar Co(III) complex. The calculated τ_4 parameter[18] of 0.39 is larger than those reported for the analogous iron complex, $[FeMe_4]^-$, (0.29),[13] and the previously reported $Co(C_6F_5)^-$ (0.12) and $Co(C_6Cl_5)^-$ (0.08) complexes.[10] The C-Co-C angles in **1** range from 92.1(1)° to 94.2(1)°. This distortion from the 90° angles of an ideal square planar complex is similar to those observed for $[FeMe_4]^-$ (89.7(7)° to 94.7(7)°),[13] $Co(C_6F_5)^-$ (90.329(7)°) and $Co(C_6Cl_5)^-$ (87.9(2)° to 92.1(2)°).[10] The Co-C bond distances in **1** (range from 1.952(2) Å to 2.012(3) Å, avg. 1.981(5) Å) are similar to those in $Co(C_6F_5)^-$ (1.985(2) Å) and shorter than those in $Co(C_6Cl_5)^-$ (2.037(4) to 2.046(4) Å, avg. 2.042(8) Å),[10] perhaps owing to the steric hindrance of the *ortho* Cl atoms. To our knowledge, only four other transition metals have been previously reported to form 4-coordinate homoleptic complexes that utilize methyl groups as ligands.[13, 19-21] A comparison of bond lengths and angles of these complexes to **1** can be found in the SI, which shows the novel cobalt complex most closely resembles the previously reported iron and manganese complexes. However, **1** appears to be the most distorted from an ideal square planar geometry, having a dihedral angle of 39.0(1)°, whereas $[FeMe_4]^-$ has a dihedral angle of 27.8(9)° and $[MnMe_4]^-$ has a dihedral angle of 26.2°.[13, 19]

As expected for a Co(III) species, **1** is X-band EPR silent due to a large zero field splitting.[7] This is in agreement with the previously reported homoleptic square planar Co(III)-aryl complexes, where there was no observed signal for both X- and Q-band EPR.[10] Hence, NMR and DFT were used to further evaluate the electronic structure and bonding of **1**. The ^1H NMR spectrum of **1** shows no signals outside of the range of 0 to 12 ppm, with the peaks corresponding to the $[Mg(acac)(NMP)]^+$ cation (there was no observation of the Me groups) of **1** found between 0 and 5 ppm at -80 °C.[10] Despite these peaks falling in the diamagnetic region, the use of low temperature Evans method NMR, utilizing α,α,α-trifluorotoluene as the internal standard, was critical in probing the spin state of **1**. Due to broad, intense solvent peaks in ^1H NMR, ^{19}F NMR was used to monitor the shift of the external solvent and internal standard. ^{19}F NMR reveals **1** to be paramagnetic, with $\mu_{eff(avg)} = 4.0(2)$ Bohr magnetons (BM, see SI for all NMR data). The assignment of the magnetic moment, utilizing atomic absorption spectroscopy to determine the concentration of **1**, is consistent with **1** being an intermediate spin $S = 1$ complex. Note that while the magnetic moment of **1** is considerably higher than the spin-only value of 2.83 BM for $S = 1$, this is not unusual for four coordinate first-row transition metal $S = 1$ complexes, where the previously reported distorted square planar $[Co(C_6F_5)]^-$ was observed to have a magnetic moment of 4.1(1) BM.[10, 22-23]

The spin state of **1** was further probed using spin-unrestricted density functional theory (DFT) calculations. Calculations of **1** were performed using the def2-TZVP basis set on all atoms. In the presence or absence of the counterion, as well as being in the gas phase or with a THF solvent model, there was almost no change in the geometry optimizations, and further calculations were carried out in the absence of the $[Mg(acac)(NMP)_4]^+$ cation (see SI). Additionally, several different functionals were tested, and all geometry optimizations for the different functionals were comparable (see SI). Therefore, B3LYP was chosen for the rest of the calculations as this functional is used in subsequent MO calculations. Supporting the $S = 1$ assignment, single-point calculations on the optimized coordinates predict the calculated $S = 1$ structure is the most energetically favored by 14 kcal/mol over the $S = 0$ ground state and by 13 kcal/mol over the $S = 2$ ground state. The calculated MO energy diagram, as well as select Frontier Molecular Orbitals (FMO) depictions, for **1** can be found in Figure 2. The following α FMOs exhibit dominant d-orbital character: occupied α27 (d_{xz}), α28 (d_{yz}), α30 (d_{xy}), and α31 (d_{z^2}), as well as unoccupied α45 ($d_{x^2-y^2}$). Here, α27 and α28 are degenerate. The following β FMOs exhibit dominant d character: occupied β28 (d_{z^2}) and β29 (d_{xy}), as well as unoccupied β32 (d_{yz}), β33(d_{xz}), and β45 ($d_{x^2-y^2}$), where β32 and β33 are degenerate. Additionally, simulated UV-vis at -80 °C is in good agreement with experimental data (see SI). Mayer bond order (MBO) and charge donation analysis were used to further probe the cobalt-methyl bonding for **1** as a $S = 1$ system (see SI). The MBO for the sum of all Co-C MBOs was found to be 2.312, with the contribution from each methyl group identical. Charge donation analysis indicates the methyl groups are strongly donating, as there is very little back donation from the cobalt center to the methyl ligands.

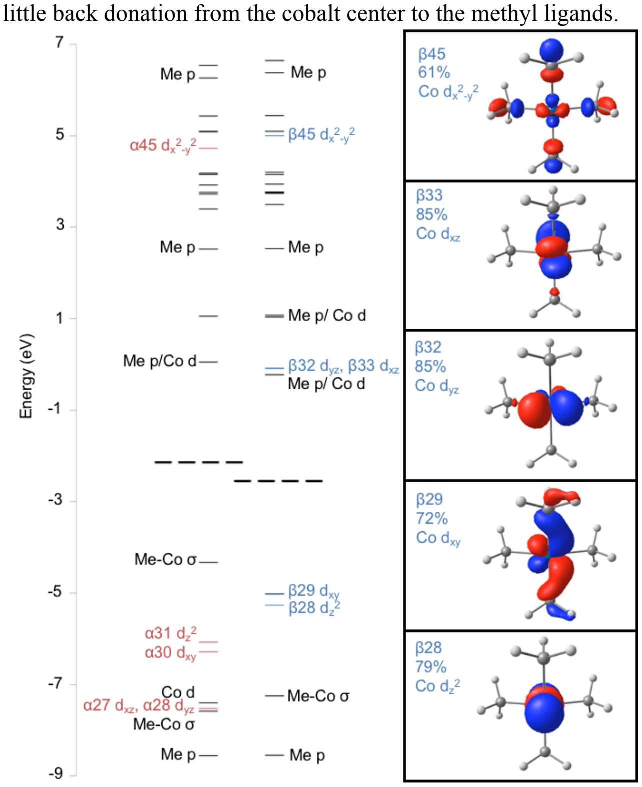


Figure 2. Calculated FMO diagrams for **1**. Additional orbital depictions are in the SI.

In summary, the synthesis and characterization of the intermediate spin, homoleptic tetramethylcobalt(III) complex $[Mg(acac)(NMP)_4][CoMe_4]$ was explored utilizing SC-XRD, NMR, and DFT. Distorted square planar $[CoMe_4]^-$ exhibits extreme thermal and moisture sensitivities, readily decomposing to a brown, paramagnetic complex. While this decomposition of $[CoMe_4]^-$ likely leads to the formation of a more reduced cobalt species, further studies are needed to understand cobalt speciation in these environments.

ASSOCIATED CONTENT

Supporting Information

Supplementary data and discussions of the experimental and theoretical methods. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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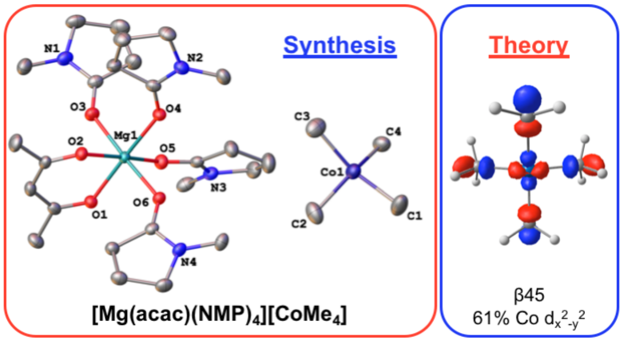
Synthesis
N1
N2
O3
O4
Mg1
O2
O5
N3
O6
O1
N4
C3
C4
Co1
C2
C1
[Mg(acac)(NMP)4][CoMe4]
Theory
β45
61% Co dx2-y2