A Rare Low-Spin Co\textsuperscript{IV} Bis(β-silyldiamide) with High Thermal Stability: Steric Enforcement of a Doublet Configuration\textsuperscript{**}

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Abstract: Attempted preparation of a chelated Co\textsuperscript{II} β-silyldiamide resulted in the unprecedented disproportionation to Co\textsuperscript{0} and a spirocyclic cobalt(IV) bis(β-silyldiamide): [Co-[(NtBu)\textsubscript{2}SiMe\textsubscript{2}]=\textsubscript{2}] (1). Compound 1 exhibited a room-temperature magnetic moment of 1.8 B.M. and a solid-state axial EPR spectrum diagnostic of a rare S = 1/2 configuration for tetrahedral Co\textsuperscript{IV}. Ab initio semicanonical coupled-cluster calculations (DLPNO-CCSD(T)) revealed the doublet state was clearly preferred (−27 kcalmol\textsuperscript{-1}) over higher spin configurations only for the bulky tert-butyl-substituted analogue. Unlike other Co\textsuperscript{IV} complexes, 1 had remarkable thermal stability, and was demonstrated to form a stable self-limiting monolayer in preliminary atomic layer deposition (ALD) surface saturation experiments. The ease of synthesis and high stability make 1 an attractive starting point to investigate otherwise inaccessible Co\textsuperscript{IV} intermediates and for synthesizing new materials.

Cobalt complexes are effective and cost-efficient alternatives to Ir- and Rh-based catalysts for a number of important C–H bond transformations,\textsuperscript{[1]} alknylations,\textsuperscript{[2]} alkylations, and arylation.\textsuperscript{[3]} Recently, high-valent Co\textsuperscript{IV} species have also been shown to affect C–H bond activation.\textsuperscript{[4]} High-valence Co-containing materials like the electrode material Li\textsubscript{2}CoO\textsubscript{2} have remarkable thermal stability, and was found to affect C–H bond activation.\textsuperscript{[9]} Co\textsuperscript{IV} bis-imide\textsuperscript{[10]} and Groysman's tricoordinate, diarylcarbene-stabilized Co\textsuperscript{IV} bis-alkoxide.\textsuperscript{[11]} While computational studies showed that the assignment of the spectroscopic oxidation state for the metal centers was ambiguous, their magnetic properties supported a S = 1/2 ground state for tetrahedral Co\textsuperscript{IV} complexes not only in light of their electronic nature but also with respect to their physico-chemical properties which might qualify them as CVD/ALD precursors.

To date, most Co\textsuperscript{IV} complexes have been prepared by 1e\textsuperscript{-} oxidation of Co\textsuperscript{III} complexes with Br\textsubscript{2}, Fe(ClO\textsubscript{4})\textsubscript{3}, or by cyclic voltammetry. The starting Co\textsuperscript{II} complexes typically comprise sterically demanding tetramido or pyrroloato macrocycles, and the resulting Co\textsuperscript{IV} species are commonly unstable above room temperature. In cases where unambiguous Co\textsuperscript{IV} species could be isolated, geometries are typically limited to square planar and square pyramidal.\textsuperscript{[8]} Macroyclic Co\textsuperscript{IV} o xo-oxogeners such as the one introduced by Wang et al. are typically more robust but still suffer from this geometrical restriction.\textsuperscript{[9]}

For d\textsuperscript{4} ions, the high-spin S = 1/2 configuration exhibits the maximum exchange energy for transition metals; thus, examples of low-spin d\textsuperscript{4} are rare. This is especially the case for tetrahedral geometries where the ligand field splitting is typically small in relation to octahedral fields. However, for Co\textsuperscript{IV}, the increased oxidation state affords larger ligand fields and so a finer energetic balance is expected between high- and low-spin electronic configurations. Interesting examples are Deng's trigonal-planar, N-heterocyclic carbene stabilized Co\textsuperscript{IV} bis-imide\textsuperscript{[10]} and Groysman's tricoordinate, diacylcarbene-stabilized Co\textsuperscript{IV} bis-alkoxide.\textsuperscript{[11]} While computational studies showed that the assignment of the spectroscopic oxidation state for the metal centers was ambiguous, their magnetic properties supported a S = 1/2 ground state in each case. More recently, a squashed-tetrahedral Co\textsuperscript{IV} tetrakis-(ketimide) Co(N=C\textsubscript{6}Bu\textsubscript{4})\textsubscript{4} was reported, but it exhibited a quartet ground state (S = 3/2).\textsuperscript{[11]}\textsuperscript{[12]} Co\textsuperscript{IV} tetraakis(1-norbornyl), Co(nor),\textsubscript{4}, has remained the only known unambiguous example of a tetracoordinate low-spin Co\textsuperscript{IV} complex for over 40 years.\textsuperscript{[12,13]}

β-Silylamines are excellent ligands to stabilize unusual coordination numbers and oxidation states for elements across the periodic table.\textsuperscript{[14]} The good thermal stability and high volatility of the well-known three-coordinate Co\textsuperscript{II} complex [Co[N(SiMe\textsubscript{3})\textsubscript{2}]]\textsubscript{2} prompted us to explore other Co β-silylamides as potential precursors for vapor phase deposition of Co-containing materials.

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Here, we report the serendipitous preparation of 1,3,5,7-tetra-tert-butyl-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disilatetra-4,4′-cobaltaspiro[3.3]heptane, [Co(NtBu)2SiMe2]4 (1), the second, unambiguous CoIV complex with a low-spin $S=\frac{1}{2}$ ground state configuration. We have implemented both experiment and theory to understand its unusual electronic nature. Finally, compound 1 has electronic properties that are complemented by physico-chemical features that set it apart from all prior reported CoIV complexes and make it especially appealing for application in ALD.

Treatment of suspended CoCl4(TMEDA) (TMEDA = tetramethylethylenediamine) with one equivalent of (LiNtBu)2SiMe2 in pentane led to a rapid change in color from ultramarine to dark brown–black. Dark gray particles were observed to precipitate from solution alongside LiCl following the disproportionation of the presumed CoII monokis(diamide) intermediate to form 1 and elemental Co0. Workup of the reaction solution afforded 10 mmol batches with ease. Satisfactory yields (60% from the ligand) were obtained from Dioxide sublimation (85 $^\circ$C/10 mTorr). The synthesis scaled well and was amenable to recrystallization from pentane at 2.6, g\text{e} = g\text{g} = 2.0."

The doublet ground state was also supported by density functional theory (DFT) calculations, as we calculated $g\text{e} = 2.4, g\text{g} = 2.0$ for the doublet state and $g\text{e} = g\text{g} = 2.0$ for the quartet and sextet states.

We turned to DFT and ab initio coupled-cluster theory to understand the electronic structure of 1. Accurate prediction of spin states with DFT is an ongoing challenge because the exact exchange-correlation functional is still unknown. While mixing a portion of exact Hartree–Fock (HF) exchange into hybrid functionals generally improves performance for closed-shell molecules, these methods are biased toward high-spin transition metal configurations. Nevertheless, all of the pure functionals (BLYP, OLYP, PBE, OPBE) and one hybrid functional (PW6B95) we employed accurately reproduced the experimental structure of 1 when a doublet ground state was considered. The quartet and sextet ground state structures did not: the quartet deviated by exhibiting a smaller ligand interplane angle ($\phi \approx 72^\circ$), and the sextet had elongated Co–N bonds (ca. 1.94 Å). The overall geometric consistency between functionals within different spin states

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Left: Solid-state structure of 1 (ellipsoids at 50% probability). Top right: Key bond lengths and angles of the two rings with the principle axis oriented vertically; bottom right: ligand plane angle $\phi$ and the $C_2$ axes when looking down the principle axis.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Yang's geometry index $r_\text{g}$ for known tetracoordinate CoIV complexes.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Left: Experimental (blue) and simulated (red) solid-state X-band EPR spectra of 1. Right: Spin density of 1 (def2-QZVPP/OPBE-D3(BJ)/def2-SVP, isosurface value = 0.02), highlighting the metal-based character of the unpaired electron.}
\end{figure}
suggested the structures were reasonable, and we proceeded with ab initio calculations for higher accuracy.

Unambiguous assignment of the doublet ground state to 1 was achieved with ab initio semicanonical coupled-cluster calculations of our best DFT-optimized structures (DLPNO-CCSD(T)/def2-TZVPP/PW6B95/def2-SVP). This recent method provides comparable performance to canonical CCSD(T), the “gold standard” of quantum chemistry, but with computational cost comparable to DFT.[23] The doublet was calculated to be 28.1 kcal mol⁻¹ and 27.1 kcal mol⁻¹ more stable than the quartet and sextet, respectively. Our prior DFT calculations had substantial errors of +22 kcal mol⁻¹ and +24 kcal mol⁻¹ for the pure and hybrid functionals, respectively. We hope that these benchmarked results of a difficult case may act as reference values in the future.

Only three Co IV complexes with unambiguous doublet ground states have been reported before: Co(nor)₄, Deng’s Co(Ndipp)₂(NHC) (dipp = 2,6-diisopropylphenyl, NHC = N-heterocyclic carbene), and Groysman’s Co(OR)₂(=CPh₃). But their apparent oxidation states are their only similarity to 1. Each belongs to a different symmetry point group (T₂ and C₃v, respectively); their bonds are distinct from the Co–N bonds in 1; Co(Ndipp)₂(NHC) and Co(OR)₂(=CPh₃) are heteroleptic and three coordinate; and the oxidation states in Co(Ndipp)₂(NHC) and Co(OR)₂(=CPh₃) were tentatively assigned alongside possible Co III resonant forms for which no precedence was found in 1. Collectively, these dissimilarities made them less useful in explaining the doublet state of 1. Despite their different ground states, consideration of Hayton’s Co(N=C(Bu)₃), was instructive as it shared the same Co–N coordination sphere as 1.

We constructed a qualitative molecular orbital (MO) diagram of the doublet and quartet configurations of 1 using DFT (Figure 4). Although both states had molecular D₃d symmetry, the molecular orbitals were mostly of lower symmetry in the D₃ point subgroup. Exceptions to this were observed for unpaired electrons: the doublet SOMO (SO = singly occupied) retained full D₃d symmetry, but the quartet SOMOs were of even lower C₁ symmetry. The doublet’s MOs were predictable from its symmetry, with the orthogonal ligand orientation stabilizing σ– and π-bonds involving the b₃(dₓz) and b₃(dₓz)₃, and b₃(dₓz,₃,₋) DOMOs (DO = doubly occupied), respectively. The corresponding π*-antibonding b₃(dₓz,₃,₋) SOMO showed π-backbonding in doublet 1, which was also observed by Mulliken spin-population analysis (0.52e on Co and 0.52e across four nitrogens). Despite their differences, we found an important parallel between the quartet state of 1 and Hayton’s Co(N=C(Bu)₃)₄. The twisted geometry and quartet ground state of Co(N=C(Bu)₃)₄ was due to π-backbonding of the unpaired electrons to the N–C π-bonds on the ligands, which was maximized with D₃d symmetry and S = 3/₂.[11] Clear π-backbonding to the N orbital was observed in the three highly distorted SOMOs of quartet 1, with more than one unpaired electron residing on the nitrogens (1.79e on Co and 1.21e across four nitrogens). Unfortunately, we could not reliably deconvolute the energetic contributions of these π-systems by energy decomposition analysis (EDA) because of the poor performance of DFT for 1.

![Figure 4](image-url) Molecular orbital diagram of 1 in the doublet (left) and quartet (right) spin state from unrestricted natural orbitals (UNOs) obtained with DFT (def2-QZVPP/OPBE-D3(BJ)/def2-SVP). DOMOs and LUMOs have D₃d symmetry, while SOMO point groups are explicitly listed. Irreducible representations, participating Co d-orbitals, and bond type are listed for each. Hydrogen, carbon, and silicon atoms have been omitted for clarity.

Steric bulk clearly played an important role in stabilizing the doublet ground state of 1, so we optimized the geometries and computed the doublet–quartet energy gaps for less bulky N-substituents in the same way as for 1 to quantify its effect (Figure 5). All the successfully optimized doublet and quartet geometries had features consistent with those in 1, and their DFT energy gaps also did not agree with the ab initio results. From the reliable ab initio calculations, we found that reducing the bulk from just tert-butyl to isopropyl made the quartet the most stable electronic configuration by a large margin (ΔE = +25 kcal mol⁻¹). The SOMOs and spin populations of the quartet states were essentially independent of steric bulk, suggesting that the ligand plane angle φ was dependent on the N-substituent more than on the extent of π-backbonding. Additionally, the geometric effect of the π-backbonding was clearly visible in the spin density plots of 1. These results together demonstrate how the tert-butyl sub-

![Figure 5](image-url) Doublet–quartet energy gaps (DLPNO-CCSD(T)/def2-TZVPP/PW6B95-D3(BJ)/def2-SVP) for different N-substituted analogues of 1 (left). Spin density (isosurface at 0.02 a.u.) and Mulliken spin populations of 1 in the doublet (middle) and quartet (right) ground states (def2-QZVPP/OPBE-D3(BJ)/def2-SVP). Hydrogen, carbon, and silicon atoms have been omitted for clarity.
stituent’s bulk was necessary to destabilize the otherwise preferred quartet ground state and it enforced the doublet ground state by orthogonal ligand arrangement. Analogues of 1 with less steric bulk are expected to have electronic structures similar to Co(N=CBu$_3$)$_4$.

We tested the robustness of 1 to examine its suitability for vapor phase deposition. As prior introduced, ALD is especially good for depositing metastable phases and exotic materials because of its self-limiting chemical mechanisms and mild operating conditions. To our knowledge, there have been no reports of either ALD or CVD of Co$^{IV}$-containing materials because of the lack of Co$^{IV}$ precursors. None of the few previously reported Co$^{IV}$ complexes displayed sufficient thermal stability or volatility. Co(nor)$_4$ decomposes at 100$^\circ$C and cannot be sublimed, Hayton’s Co(N=C(Bu)$_3$)$_4$ decomposes in solution at ambient temperature, Deng’s Co(=N-dipp)$_4$(NHC) undergoes reductive C–H bond activation at 50$^\circ$C, while Groysman’s Co(OR)$_2$(=CPh$_2$) is likely nonvolatile due to its high molecular weight and numerous phenyl groups.

We quantitatively evaluated the suitability of 1 as a precursor with respect to its thermal stability and volatility by thermogravimetric analysis (TGA) and differential thermal calorimetry (DSC). When a 10.1 mg sample was heated with a linearly increasing temperature ramp, a clean single-step mass loss was observed between 150–230$^\circ$C leaving behind a small residual mass of 3.2%, indicating that most of the sample evaporated during the experiment (Figure 6a). TGA can also be used to efficiently estimate vapor pressure by employing the Langmuir equation, and the temperature at which 1 displays 1 torr of vapor pressure was estimated with a Clausius–Clapeyron model to be (150.4 ± 0.1)$^\circ$C (Figure 6b). DSC revealed the melting point to be 143$^\circ$C and the onset of decomposition (defined as 5% of the maximum of the first exothermic event) to be 197$^\circ$C. The “thermal range” between the 1 torr vapor pressure temperature and the decomposition temperature is often a practical and reliable benchmark of a compound’s practicality as an ALD precursor. With a thermal range spanning roughly 47$^\circ$C, compound 1 represents a promising precursor candidate for ALD.

To contextualize the performance of 1, we subjected two recently reported Co$^{III}$ precursors to thermal analysis: namely CoCl$_2$(TMEDA)$_2$ and Co(DAD)$_2$ (DAD = tert-butylidiazadienyl) (see the Supporting Information). We applied our recently developed “Figure of merit” $\sigma$ that takes key parameters such as thermal range, vapor pressure, and extent of decomposition during TGA into account to quantitatively compare precursors (Table S2). A positive Figure of merit indicates the suitability of a precursor while negative indicates a poor candidate. With $\sigma = 35$, complex 1 ranks between [Co(DAD)$_2$] ($\sigma = 64$) and [CoCl$_2$(TMEDA)] ($\sigma = -2$) where the weak performance of the latter originates from its low volatility. Therefore, 1 was not only competitive with successfully applied Co$^{III}$ precursors but, to the best of our knowledge, represents the only known potential Co$^{IV}$ precursor candidate.

The most important characteristic of an ALD precursor is the ability to form a stable self-limiting monolayer on a surface. After all reactive surface sites have undergone a reaction with precursor molecules, no further adsorption should occur, allowing conformal and uniform atomic layer deposition to take place during the next self-limiting reaction. Employing a quartz crystal microbalance (QCM) in our home-built ALD tool, we investigated the potential for 1 to fulfill this basic yet critical requirement. The precursor was heated to 135$^\circ$C for delivery and the QCM crystal was heated to 150$^\circ$C for saturation experiments. Compound 1 demonstrated self-limiting adsorption on alumina with a mass gain of (49.2 ± 0.3) ng cm$^{-2}$ that was stable over roughly 35 minutes (Figure 6c). This encouraging initial result motivated us to begin developing ALD processes with 1 in ongoing research.

In summary, a thermally stable, volatile, homoleptic, spirocyclic Co$^{IV}$ bis(β-silyldiamide) was synthesized in a facile one-step salt-metathesis exploiting Co$^{II}$ disproportionation. Experiment and theory confirmed that it exhibits a rare low-spin d$^5$ doublet configuration enforced by the steric bulk and geometric rigidity of its ligands. The remarkable stability of 1 makes it a promising precursor for vapor deposition, and its ability to form a stable self-limiting monolayer makes it a promising ALD precursor. Beyond this, 1 represents a simple, inexpensive, and accessible starting material for further high-valent Co$^{IV}$ chemistry to be explored.

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Conflict of interest

The authors declare no conflict of interest.

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