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Synthesis, Characterization, and Thermal Properties of N-alkyl β -Diketiminate Manganese Complexes

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S Supporting Information

ABSTRACT: A series of N,N'-dialkyl- β -diketiminato manganese(II) complexes was synthesized and characterized by single crystal X-ray diffraction, UV-vis and FTIR spectroscopy, and then assayed for volatility, thermal stability, and surface reactivity relevant to vapor-phase film growth processes. Bis(N,N'-dimethyl-4-amino-3-penten-2-imine) manganese(II), 1, and bis(N-N'-diisopropyl-4-amino-3-penten-2-imine) manganese(II), 2, specifically, emerge as the most promising candidates, balancing volatility (sublimation temperatures < 100 °C at 100 mTorr) with coordinative unsaturation and reactivity, as revealed by rapid release of ligand in the presence of a silica surface. Good correlation is observed between buried volume calculations and relative surface reactivity data, indicating that metal availability resulting from sterically open ligand alkyl substituents increases surface reactivity. The thermal stability, volatility, and reactivity exhibited by these compounds render them



promising precursors for the growth of manganese oxide films via vapor-phase growth processes.

INTRODUCTION

Thin manganese oxide films are of interest for a plethora of applications, ranging from energy storage as battery cathodes,¹⁻⁵ to layered materials for ultracapacitors^{6,7} due to their rich redox chemistry, low cost, and earth abundance. Note that there is an increasing need for high-quality thin films in the development of these microsystems. To this end, many techniques have been developed for the synthesis of manganese oxide thin films, including solution-based processes (electro-deposition,^{8,9} sol-gel,¹⁰ dip-coating^{11,12}) and vapor-phase processes (chemical vapor deposition,^{13,14} molecular beam epitaxy,^{15,16} pulsed layer deposition¹⁷). Of particular interest are chemical vapor deposition (CVD) and related atomic layer deposition (ALD) processes, which provide high levels of control over film thickness, tunability through metal-organic precursor choice, conformal coating (they are not line-of-sight growth processes), and scalability. Additionally, ALD offers selflimiting surface reactivity that provides smooth, layer-by-layer film growth (<1 nm roughness)¹⁸ under relatively mild conditions (<300 °C) and with atomic precision. Both CVD and ALD processes have been adopted industrially in the microelectronics industry,¹⁹⁻²¹ making them ideal for highthroughput thin film syntheses.

A number of modalities are known for the vapor-phase growth of manganese oxide films by CVD/ALD using a variety of commercially available precursors (Table 1). The effects of substrate,²² coreactant,^{1,23,24} reaction temperature,^{25,26} and annealing conditions^{27,28} have all been investigated, resulting in promising degrees of control over manganese oxide (MnO_x) composition (MnO, Mn₃O₄, Mn₂O₃, MnO₂, etc.) after parameter optimization. Significant advances have also been made by $Winter^{29-32}$ and $Gordon^{33,34}$ (Table 1) in the

Table 1. Manganese Precursors Evaluated for ALD Growth Processes

compound	ALD process	reference
$Mn(thd)_3^a$	yes	35
$Mn(CpEt)_2^{b}$	yes	26
CpMnMe(CO) ₃ ^c	yes	23
$Mn_2(CO)_{10}$	yes	13, 25
$Mn(^{t}Bu-MeAMD)_{2}^{d}$	no	33, 34
$Mn_2(\mu$ - ^{<i>i</i>} Pr-MeAMD) ₂ (η ² - ^{<i>i</i>} Pr-MeAMD) ₂ ^{<i>e</i>}	no	34
$Mn(^{t}Bu_{2}COCN^{t}Bu)_{2}^{f}$	no	31
$[Mn(Me^{t}BuCOCN^{t}Bu)_{2}]_{2}^{g}$	yes	31
Mn(^t BuNNCHCHN ^t Bu) ₂ ^h	no	30
$Mn(NMe_2NNCHCHN^tBu)_2^{i}$	no	30
$Mn(^{t}Bu_{2}DAD)_{2}^{j}$	no	36

^{*a*}thd = 2,2,6,6-tetramethyl-3,5-heptanedione. ^{*b*}CpEt = ethylcyclopentadiene. ^cCp = cyclopentadiene. ^{dt}Bu-MeAMD = N_iN' -di-tertbutylacetamidinate. e_i Pr-MeAMD = N,N'-diisopropylacetamidinate. $f^{t}Bu_{2}COCN^{t}Bu = 3 \cdot ((tert-butyliminomethyl) \cdot 2, 2, 4, 4 \cdot tetramethylpen \cdot 1)$ tan-3-oxide. ^gMe^tBuCOCN^tBu = 1-(*tert*-butylimino)-2,3,3-trimethylbutan-2-oxide. ^{ht}BuNNCHCHN^tBu = 1,5-di-*tert*-butyl-1,2,5-triazapentadiene. ⁱNMe₂NNCHCHN^tBu = 1-tert-butyl-5-dimethylamino-1,2,5triazapentadiene. ^{*j*}DAD = 1,4-di-*tert*-butyl-1,3-diazadiene.

development of designer ALD precursors, although these studies have primarily focused on growth of metallic films.

One class of ligands that lends itself well to vapor deposition processes is the β -diketiminate ligand (NacNac, Figure 1). β -Diketiminates provide a high level of ligand tunability, in both the inner and outer coordination sphere, and have been

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Figure 1. β -Diketonate (AcacH), β -diketiminate (NacNacH) ligand precursors, and example of a dimeric manganese complex resulting from extreme steric hindrance of *N*-Ar substituents.²⁰

previously shown to induce volatility in alkali earth metals and lanthanides.²⁹ They are closely analogous to, but more sterically encumbered than, acetylacetonate derivatives (e.g., thd in Table 1) that are currently used for the growth of manganese oxide films.

While there is a wealth of knowledge about the chemistry and reactivity of β -diketiminate coordination complexes,^{37–} there are surprisingly few reported examples for manganese.^{40–45} Those previously described utilize either R' = R''= aryl or N-aryl substituents (Figure 1) to electronically or sterically stabilize the manganese(II) center. In the case of bulky N-2,6-ⁱPr₂C₆H₃ (N-Dipp) substituents, attempts to produce bis(diketiminato) complexes fail due to steric crowding at the metal center, and instead form dimeric diketiminato manganese μ -halido complexes (Figure 1).⁴² Additionally, while N-aryl β -diketiminates have been widely studied, they are undesirable for use as vapor deposition precursors due to potential $\pi - \pi$ packing interactions in the solid state that often decrease volatility.⁴⁶ Alkyl N-substituted β diketiminates, however, can be leveraged to increase both volatility and metal center reactivity due to their generally lower steric demands. In the case of metallic copper film deposition for example, extensive studies have shown that copper alkyl β diketiminates are highly competent for copper ALD.⁴⁷⁻⁴⁹ Firstrow transition metal alkyl N-substituted β -diketiminates compounds are well-known in the literature, although the manganese congeners have remained heretofore unreported.^{50,51} Thus, the synthesis and characterization of Nalkyl β -diketiminato manganese compounds presents an attractive approach for the vapor-phase growth of manganese oxide containing films.

With the aim of providing new precursors for manganese oxide film growth processes, the synthesis of new volatile and thermally stable β -diketiminate manganese complexes was pursued. This work presents a systematic study of a series of *N*-alkyl β -diketiminate manganese(II) complexes. Along with their synthesis and characterization, thermogravimetric analysis and solution-phase reactivity data indicate promising performance for vapor deposition processes.

RESULTS AND DISCUSSION

The synthesis of β -diketimine ligands was performed according to general literature procedures (see the Supporting Information for full synthetic details). Metalation was achieved by first deprotonating the corresponding *N*-alkyl β -diketimine at 0 °C with "BuLi, followed by addition of the resulting Li-ligand solution to a suspension of MnCl₂ in tetrahydrofuran or diethyl ether (Scheme 1). Pure products are easily obtained by crystallization from pentane or toluene, in low to moderate yields (18–60%). Compound 1 is poorly soluble in aliphatic hydrocarbons, but readily dissolves in toluene and ether, while





compounds 2-4 exhibit good solubility in all common hydrocarbon and etheric solvents. Purification by vacuum sublimation (see Table 3 for conditions) is also possible and was performed for all compounds. Note that 1 is extremely air/ moisture sensitive, but this sensitivity decreases as the steric bulk around the metal increases, such that complexes 3 and 4 are fairly stable under atmospheric conditions for hours in the solid state before decomposition is observed (compared to seconds for 1). Compounds 1-4 were characterized by UV-vis and FTIR spectroscopies (see the Supporting Information, Figures S1 and S2, respectively) and elemental analysis, and single crystals suitable for X-ray diffraction were grown from concentrated pentane (compounds 2-4) or toluene (compound 1) solutions at $-40 \,^{\circ}\text{C}$ (Figure 2). While these reactions as described provide modest yields of 1-4 (18-60%) that are less than the large amounts (5-10 g) of material typically needed for optimizing film deposition processes, these reactions are easily scalable and in this work have been successfully scaled up to the multigram scale.

Single crystal X-ray diffraction analysis confirms the monomeric nature of $bis(\beta$ -diketiminate) manganese(II) complexes 1-4 (Figure 2, Table 2). For all four compounds, it will be seen that the β -diketiminate ligands act as bidentate ligands and coordinate in a N_iN' -chelating fashion, as indicated by both the atomic connectivity and electron delocalizationinduced planarity of the NCCCN backbone in the crystal structures. Other ligand bond lengths and angles are similar to those of previously reported, related non-manganese compounds.³⁷ While all structures exhibit some distortion in the tetrahedral coordination geometry due to bidentate bonding of the ligand that is well-known for four-coordinate Mn(II), compound 1 is by far the most distorted, with a dihedral angle of 72.5° . Complexes 2-4 display modest distortion, with dihedral angles of 89.0°, 87.9°, and 85.8°, respectively. For the methyl variant, compound 1, higher symmetry is also observed in the crystal structure, since it crystallizes in the orthorhombic *Pbcn* space group, while the rest of the series, compounds 2-4, crystallize in $P2_1/n$ (see Table S1 for additional crystallographic data and refinement parameters). This is attributed to the decreased degrees of freedom for the methyl substituent compared to the branched isopropyl, tert-butyl, and cyclohexyl derivatives. The average Mn-N bond lengths increase as 1 $(2.087(1) \text{ Å}) < 2 (2.103(6) \text{ Å}) < 4 (2.125(1) \text{ Å}) \sim 3 (2.129(2))$ Å), resulting from incrementally increased crowding around the metal center (Table 2). These values are slightly elongated compared to known N-aryl β -diketiminato manganese(II) halide dimers $[(2,6-iPr_2C_6H_3)NacNacMnCl]_2$ Mn-N = 2.082(1) Å⁴³ and $[(2,6^{-i}Pr_2C_6H_3)NacNacMnI]_2$ Mn–N = 2.067(2) Å,⁴² again, likely reflecting the increased steric repulsion of a second β -diketiminate within the primary coordination sphere. For related bis(amidinato) manganese(II)



Figure 2. Single crystal X-ray structures for (A) complex 1; (B) complex 2; (C) complex 3; (D) complex 4. Thermal ellipsoids at 50% probability.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1-4

1			
Mn1-N1	2.0873(11)	Mn1-N2	2.0861(10)
N1-Mn-N2	91.51(4)	N1-Mn-N1'	108.08(6)
N2-Mn-N2'	110.64(6)		
2			
Mn1-N1	2.1010(6)	Mn1-N2	2.0978(6)
Mn1-N3	2.0948(6)	Mn1-N4	2.1155(7)
N1-Mn1-N2	96.93(2)	N3-Mn1-N4	96.82(3)
N1-Mn1-N3	120.21(2)	N1-Mn1-N4	110.84(2)
N2-Mn1-N3	119.93(2)	N2-Mn1-N4	112.80(2)
3			
Mn1-N1	2.1282(18)	Mn1-N2	2.1321(18)
Mn1-N3	2.1256(18)	Mn1-N4	2.1309(18)
N1-Mn1-N2	99.32(7)	N3-Mn1-N4	99.29(7)
N1-Mn1-N3	114.26(7)	N1-Mn1-N4	113.83(7)
N2-Mn1-N3	114.22(7)	N2-Mn1-N4	116.78(7)
4			
Mn1-N1	2.1264(12)	Mn1-N2	2.1246(12)
Mn1-N3	2.1295(12)	Mn1-N4	2.1194(12)
N1-Mn1-N2	94.12(5)	N3-Mn1-N4	94.27(5)
N1-Mn1-N3	110.36(5)	N1-Mn1-N4	115.87(5)
N2-Mn1-N3	116.41(5)	N2-Mn1-N4	126.53(5)

compounds, however, very similar Mn–N bond lengths are observed $[{PhC(NAr)_2}_2Mn] = 2.113(3)$ Å (Ar = 2,6-ⁱPr_2C_6H_3)⁵⁵ and $[{MesC(N^iPr)_2}_2Mn] = 2.085(7)$ Å.⁵⁶

Slight puckering of the manganese out of the ligand plane is observed for complexes **2** and **4** (0.294 and 0.317 Å out of plane, respectively), which is well-documented in metal β -diketiminato complexes where there is repulsion between N-substituents and the metal.³⁹ This puckering of the metal center is insufficient to disrupt the expected trends evident in the buried metal center calculations (*vide infra*). In the case of compounds **2** and **4**, hydrogen atoms on the *N*-isopropyl and cyclohexyl γ -carbons appear to approach the metal center (2.80–2.88 Å), resulting in its subsequent dislocation. Whether these hydrogens are oriented due to weak interaction with the metal center or geometric packing preferences of the 2° alkyl substituted ligands is unclear.

The effects of these structural distortions are also seen in the electronic characterization of 1–4. An Evans' method analysis^{57,58} of complexes 1–4 yields $\mu_{eff} = 5.84-5.95 \mu_B$ (see Table 3 for exact values), all in excellent agreement with the

Table 3. Physical and Volatility Characterization Data for Complexes 1–4

compound	μ_{eff}	% $V_{\rm bur}$	sublimation temp (°C) ^a	melting point (°C)	TGA onset (°C)
1	5.84	22.2	75	180	212
2	5.95	32.0	90	109	263
3	5.94	36.7	110	200	280
4	5.85	42.8	125	190	326

^aAt 100 mTorr.

value $\mu_{\text{eff}} = 5.92 \ \mu_{\text{B}}$ expected for high spin $S = 5/2 \ \text{Mn}^{2+}$. UV– visible spectroscopy of the yellow/orange compounds (Figure S1) reveals two main absorption features centered at 311–315 and 380–390 nm, both attributable to ligand-centered charge transfer-to-metal excitations, in agreement with previous reports.⁵⁹ For compounds 1 and 3, the band around 315 nm is of higher intensity ($10^4 \text{ cm}^{-1} \text{ M}^{-1}$) with lower absorption for the second feature ($10^3 \text{ cm}^{-1} \text{ M}^{-1}$), while compounds 2 and 4 follow the opposite trend, with more intense red-shifted features. These differences can be attributed to displacement of the metal center out of the ligand plane, resulting in decreased metal–ligand orbital overlap for compounds 2 and 4, and subsequent shifting of the ligand orbital energies. Comparable phenomena are well-known for the Q peaks in structurally similar metalloporphyrin systems.⁶⁰

In an attempt to quantify the steric congestion around the metal centers as a function of N-alkyl substituent, buried volume calculations were performed.⁶¹ Buried volume $(V_{\rm bur})$ has been proposed as a more accurate descriptor for metal accessibility, specifically for catalytic systems, compared to classical cone angle measurements as it is generalizable to virtually any ligand environment.⁶² Recent studies have also used such computations to gain insight into coordination sphere bulk relative to surface reactivity for molybdenum ALD precursors.⁶³ Calculations and steric maps were computed using SambVca 2.0 software, and were performed using atomic coordinates from the single crystal X-ray diffraction data, with a radius of 7 Å and mesh size of 0.1 Å. This radius was chosen such that the entire coordination sphere around the manganese was considered. Hydrogen atoms were not included in the calculation. The resulting $V_{\rm bur}$ values are shown in Table 3, and as expected, 1 exhibits the most open metal site by far, with $V_{\rm bur}$ = 22.2%. For substituents R = i Pr, t Bu, and Cy, the V_{bur} = 32.0, 36.7, and 42.8%, respectively. Note that these buried volumes agree very well with expected trends based on increasing sterics from $1^{\circ} < 2^{\circ} < 3^{\circ}$ alkyl substituents, except for R = Cy, which deviates due to the bulkiness of the cyclic C6 rings wrapping around the metal center. Comparing the 2° alkyl substituents (isopropyl and cyclohexyl), this additional congestion also explains the increased air/water stability of compound 4 over 2 (vide supra), since the large hydrophobic ligands would be expected to impede diffusion of water or oxygen to the reactive metal center.

Thermogravimetric analysis (TGA) of compounds 1-4 was next used to evaluate the candidacy of these compounds for film vapor deposition processes. Measurement of TGA profiles in a glovebox reveals a single mass loss indicative of smooth volatilization, without evidence of any decomposition processes and <5% residue (Figure 3A; onset temperatures are listed in Table 3). Onset temperatures were extrapolated from the tangential intersection of the initial mass and midpoint of the mass loss plot, using the manufacturer's Pyris software. Compound 1 exhibits the lowest onset temperature, beginning at ~212 $^{\circ}$ C; the onset temperature then increases linearly with molecular weight for this series of compounds (Figure 3B). Note that this also correlates well with the increased temperature required for sublimation as molecular weight increases (Table 3). Measurement of melting points in sealed capillaries for compounds 1-4 (Table 3) reveals a less intuitive trend, where 2 exhibits the lowest melting temperature, resulting from a combination of poor crystal packing (low density) and low molecular weight (for calculated densities from crystal packing, see Table S1). Compound 1 exhibits the



Figure 3. (A) TGA profiles of complexes 1–4. (B) Correlation of volatilization onset temperature with molecular weight.

highest melting point, attributable to its highly ordered crystal packing and fewer degrees of vibrational freedom. Note also that all compounds are stable up to 200 °C, with no obvious sign of decomposition, based on heating compounds in a sealed capillary for 1 h. For 2, quantitative sublimation of 0.5 g of material was successfully performed. The sublimed material was then recrystallized and the resulting single crystals had an identical unit cell as 2, confirming that no decomposition or other degradative process had occurred. On the basis of these results, this series of β -diketiminate compounds displays promising volatility and thermal stability for vapor deposition processes.

Once volatility and thermal stability were established for this series of manganese β -diketiminate complexes, solution-phase reactivity as a model for ALD-like film growth processes was probed using ¹H NMR. Recent reports utilize solution-phase reactivity, in conjunction with spectroscopic characterization tools, to elucidate operative mechanisms in ALD processes,⁶⁴ and here, this technique was employed to inform relative rates of surface reactivity (Scheme 2). In a typical experiment, in a glovebox, the yellow/orange manganese precursor was combined with high surface area silica (400 m^2/g) in a J-Young NMR tube and hexamethylbenzene was added as an internal standard, all in C₆D₆. The mixture was then vigorously agitated and the protonolytic release of ligand monitored as a function of time (Scheme 2, Figure 4). Over time, the silica turned bright yellow and the supernatant solution became colorless, visually indicating manganese chemisorption on the surface. Note that, in the case of 1 (Figure 4), ligand concentration initially increases, but then begins to decrease over time. It is hypothesized that this results from physisorption of the free Me₂NacNacH ligand imine/amine functionalities on the weakly acidic surface (via hydrogen bonding) as it is produced from the protonolytic reaction of compound 1 with the surface (Scheme 2). This was confirmed by a control experiment which found that, with only free ligand and silica, the concentration of free Me₂NacNacH decreased over time as it adsorbed onto the surface. While any rate data for reaction of compound 1 is obscured by ligand consumption, the reaction solution becomes colorless within 2 h, significantly more rapidly than for compound 2. For the remaining compounds, the apparent rate of ligand release, given by $t_{1/2}$, increases in the order of 4 < 3 < 2 (Figure 4). Comparing the half-lives with the buried volume calculations (vide supra), excellent agreement is observed, such that less buried volume correlates with increased surface reactivity for **2** (V_{bur} = 32.0%, $t_{1/2}$ = 19 min), **3** (V_{bur} = 36.7%, $t_{1/2} = 31$ min), and 4 ($V_{\text{bur}} = 42.8\%$, $t_{1/2} = 230$ min). Note that the reactivity of 4 appears to decrease significantly more than expected, possibly reflecting the slower diffusion of





Figure 4. Solution-phase reaction of compounds $1{-}4$ with silica in $C_6 D_6.$

the more sizable $Cy_2NacNacH$ molecule away from the surface. Thus, buried volume calculations serve as a good predictor of protonolytic surface reactivity. In terms of correlating this solution-phase reactivity with ALD processes, the facile reactivity of compound **1** suggests the greatest potential for vapor-phase processes. Although physisorption of free ligand could in principal cause carbon/nitrogen contamination of films, the elevated temperatures of deposition will likely minimize this physisorptive phenomenon. Complexes **2** and **3** also exhibit good reactivity, and, due to the easier handling than **1**, are posed as potentially applicable to synthesis of manganese oxide films via vapor-phase or solution-phase growth processes.

Next, the oxidation/hydroxyl regeneration half-cycle of Scheme 2 was investigated. To this end, the chemisorbed products of the complexes 1 and 2 with silica ($1/SiO_2$ and $2/SiO_2$) were isolated by filtration, washed with pentane, and dried *in vacuo*. Exposure to water results in an immediate color change from yellow to tan. Quantification of released ligand for this step was attempted, but was obscured by the aqueous hydrolysis of the β -diketimine in the presence of excess water. X-ray photoelectron spectroscopy (XPS) was next applied to



Figure 5. Mn 2p, O 1s, and Mn 3s XPS spectra of (A) 1/SiO₂ and (B) 2/SiO₂.

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probe the surface species on the hydrolyzed powders (Figure 5). Overlapping binding energies complicate the assignment of manganese oxidation states based solely on binding energy; however, the Mn 3s splitting energy is known to correlate with oxidation state. Thus, for Mn-O species, Mn 3s splitting energies fall between 5.9 -5.7 eV for Mn(II), 5.6-5.2 eV for Mn(III), and less than 5.0 for Mn(IV).65,66 Analysis of the present tan powders by XPS (Figure 5) reveals ΔE_{3s} of 5.8 and 6.0 eV for 1/SiO₂ and 2/SiO₂, respectively, indicating the presence of predominantly Mn(II) species on the surface. Additionally, the presence of the "shake up" peak in the Mn $2p_{3/2}$ spectra around 645 eV is consistent with the assignment of Mn(II) species.⁶⁷⁻⁷⁰ The presence of the extra feature at 654.7 eV in the Mn $2p_{1/2}$ peak of $2/SiO_2$ as well as the additional higher energy 531.9 eV peak in the O 1s spectrum may indicate the presence of small amounts of a higher oxidation state Mn species on the surface. This may reflect partial oxidation during hydrolysis due to the slower reaction of the bulkier O-Mn-ⁱPrNacNac environment compared to that of the methyl analogue. The exact nature of the manganese oxygen species (e.g., Mn-O-Mn, Mn-OH) cannot be unambiguously delineated from the O 1s peak due to overlapping Si-O features.⁷¹ Some nitrogenous species (<2%, Figures S11 and S12) are also observed by XPS, likely resulting from ligand physisorption to the surface. The binding energy of these peaks (399 eV) agrees well with known energies for imine N species, suggesting free ligand binding to the surface.^{72,73} Slightly increased nitrogenous species are observed for 1/SiO₂ (1.2%) than for 2/SiO₂ (0.8%), reflecting the strong free ligand physisorption of 1 to the silica surface that was observed by ¹H NMR in the kinetic experiments. Note that, as discussed above, ligand physisorption, and subsequent nitrogen contamination, should be remedied by the elevated temperatures of typical vapor deposition processes. These results prove the competency of both complexes 1 and 2 for solution-phase reactivity analogous to that of ALD half-cycles.

The chemistry of β -diketiminate manganese(II) compounds has been expanded through the synthesis and characterization of a series of N-alkyl variants, which were assessed for their potential as vapor deposition precursors. Structural and electronic characterization by single crystal X-ray diffraction as well as UV-vis reveals that steric factors are the main driver in observed chemical/physical trends, i.e., increased air/water stability, metal puckering from the ligand plane, and dihedral angles in the coordination sphere. All of these new compounds exhibit a single, clean volatilization event in TGA profiles, with onset temperatures scaling linearly with molecular weight, and good thermal stability observed up to 200 °C, proving that β diketiminates induce volatility in manganese compounds. In addition to volatility and thermal stability, the solution-phase reactivity in models for ALD half-cycles was explored, and for the first half-cycle of protonolytic chemisorption on silica, reactivity is found to correlate well with buried volume computation, though ligand diffusion may have some effect on apparent rates. Hydrolysis of 1/SiO₂ and 2/SiO₂ mimicks the second ALD half-cycle, and clean Mn(II)-O surface species were observed by XPS, in good agreement with NMR results. Thus, preliminary evaluations were utilized to identify likely candidates for vapor deposition of manganese oxide films from a series of N-alkyl β -diketiminates, demonstrating the viability of this ligand set for manganese vapor deposition precursors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02476.

Crystallographic data and structure refinement details for 1-4 (Table S1); UV-visible spectra of 1-4 (Figure S1); FTIR spectra of 1-4 (Figure S2); buried volume maps for 1-4 (Figure S3); time-lapsed ¹H NMR spectra of $1-4/SiO_2$ (Figures S4–S7); selected XPS peaks for SiO₂, $1/SiO_2$, and $2/SiO_2$ (Table S2); survey and N 1s XPS spectra of SiO₂, $1/SiO_2$, and $2/SiO_2$ (Figures S8–S12); bond lengths and bond angles for the X-ray crystal structure of 1 (Tables S3 and S4); bond lengths and bond angles for the X-ray crystal structure of 3 (Tables S7 and S8); bond lengths and bond angles for the X-ray crystal structure of 4 (Tables S9 and S10) (PDF)

Accession Codes

CCDC 1576501–1576504 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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