Supplementary Material for

Synthesis of Tetraphenylporphyrinate Manganese(III) Siloxides by Silyl Group Transfer from Silanethiols

Daniel J. Meininger, Zeiph Kasrawi, Hadi D. Arman, and Zachary J. Tonzetich*

Department of Chemistry, University of Texas at San Antonio, San Antonio, TX, USA

zachary.tonzetich@utsa.edu

Contents	Pages
Figure S1. ^1H NMR spectrum of $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$.	S2
Figure S2. ^1H NMR spectra of $[\text{Mn}(\text{OAc})(\text{TPP})]$ and $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$.	S3
Figure S3. ^1H NMR spectrum of $[\text{Mn}(\text{OSiPh}_3)(\text{TPP})]$.	S4
Figure S4. Electronic absorption spectrum of $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$.	S5
Figure S5. Electronic absorption spectrum of $[\text{Mn}(\text{OSiPh}_3)(\text{TPP})]$.	S6
Figure S6. HRMS of $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$.	S7
Figure S7. HRMS of $[\text{Mn}(\text{OSiPh}_3)(\text{TPP})]$.	S8
Table S1. Crystallographic data and refinement parameters.	S9

Figure S1. 500 MHz ^1H NMR spectrum of $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$ in benzene- d_6 showing peak assignments. Asterisk denotes resonance due to $\text{C}_6\text{D}_5\text{H}$. The peaks between 0 and 5 ppm include resonances attributable to toluene and pentane from recrystallization.

Figure S2. Overlay of the 500 MHz ^1H NMR spectra of $[\text{Mn}(\text{OAc})(\text{TPP})]$ (red) and $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$ (blue) in benzene- d_6 showing the upfield shift of the pyrrolic resonance upon substitution of the acetate group for the siloxide.

Figure S3. 500 MHz ^1H NMR spectrum of $[\text{Mn}(\text{OSiPh}_3)(\text{TPP})]$ in benzene- d_6 showing peak assignments. Asterisk denotes resonance due to $\text{C}_6\text{D}_5\text{H}$. The cross denotes peaks due to excess HSSiPh_3 .

Figure S4. Electronic absorption spectrum of $[\text{Mn}(\text{OSi}^i\text{Pr}_3)(\text{TPP})]$ in toluene.

Figure S5. Electronic absorption spectrum of [Mn(OSiPh₃)(TPP)] in toluene.

Figure S6. HRMS (APCI, negative mode) of $[Mn(OSi^iPr_3)(TPP)]$.

Figure S7. HRMS (APCI, negative mode) of $[\text{Mn}(\text{OSiPh}_3)(\text{TPP})]$.

Table S1. Crystallographic data and refinement parameters for [Mn(OSi^{*i*}Pr₃)(TPP)] and [Mn(OSiPh₃)(TPP)].[§]

Compound	[Mn(OSi ^{<i>i</i>} Pr ₃)(TPP)]	[Mn(OSiPh ₃)(TPP)]
Empirical formula	C ₅₃ H ₄₉ MnN ₄ OSi	C ₆₂ H ₄₃ MnN ₄ OSi
Formula weight (g/mol)	840.99	943.03
Temperature (K)	98(2)	293(2)
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Unit cell dimensions (Å)	<i>a</i> = 12.482(3)	<i>a</i> = 11.953(5)
	<i>b</i> = 13.124(4)	<i>b</i> = 13.955(6)
	<i>c</i> = 14.834(3)	<i>c</i> = 16.102(8)
	α = 75.206(17)	α = 101.262(8)
	β = 65.422(13)	β = 109.513(6)
	γ = 85.016(16)	γ = 93.035(7)
Volume (Å ³)	2136.1(9)	2463(2)
<i>Z</i>	2	2
Calculated density (g/cm ³)	1.308	1.272
Absorption coefficient (mm ⁻¹)	0.382	0.340
<i>F</i> (000)	884	980
Crystal size (mm)	0.35 × 0.34 × 0.05	0.2 × 0.2 × 0.2
Θ range	2.38 to 26.00°	2.255 to 25.500°
Limiting indices	$-15 \leq h \leq 15$,	$-14 \leq h \leq 14$,
	$-16 \leq k \leq 16$,	$-12 \leq k \leq 16$,
	$-16 \leq l \leq 18$	$-19 \leq l \leq 19$
Reflections collected / unique	14376 / 8362	16310 / 9053
	[<i>R</i> _{int} = 0.0693]	[<i>R</i> _{int} = 0.0612]
Completeness to Θ	99.4%	98.8%
Absorption correction	multi-scan ABSCOR	multi-scan ABSCOR
Min. and max transmission	0.731 and 1.000	0.851 and 1.000
Data / restraints / parameters	8362 / 0 / 541	9053 / 0 / 622
Goodness-of-fit on <i>F</i> ²	1.010	1.042
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0563,	<i>R</i> ₁ = 0.0539,
	w <i>R</i> ₂ = 0.1257	w <i>R</i> ₂ = 0.1270
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0685,	<i>R</i> ₁ = 0.0610,
	w <i>R</i> ₂ = 0.1352	w <i>R</i> ₂ = 0.1330
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.471 and -0.531	0.390 and -0.437

[§]Refinement method was full-matrix least-squares on *F*²; wavelength = 0.71073 Å. *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; w*R*₂ = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.