Supplementary Material for

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

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Figure S1. 500 MHz $^1$H NMR spectrum of [Mn(OSiPr$_3$)(TPP)] in benzene-d$_6$ showing peak assignments. Asterisk denotes resonance due to C$_6$D$_5$H. The peaks between 0 and 5 ppm include resonances attributable to toluene and pentane from recrystallization.
Figure S2. Overlay of the 500 MHz $^1$H NMR spectra of [Mn(OAc)(TPP)] (red) and [Mn(OSi$_3$Pr$_3$(TPP)] (blue) in benzene-$d_6$ showing the upfield shift of the pyrrolic resonance upon substitution of the acetate group for the siloxide.
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Figure S5. Electronic absorption spectrum of [Mn(OSiPh₃)(TPP)] in toluene.
Figure S6. HRMS (APCI, negative mode) of [Mn(OSi^iPr_3)(TPP)].

\[ [M]^- = 840.3080 \]
Figure S7. HRMS (APCI, negative mode) of [Mn(OSiPh₃)(TPP)].
Table S1. Crystallographic data and refinement parameters for [Mn(OSiPr$_3$)(TPP)] and [Mn(OSiPh$_3$)(TPP)].

| Compound | [Mn(OSiPr$_3$)(TPP)] | [Mn(OSiPh$_3$)(TPP)] |
|----------|----------------------|-----------------------|
| Empirical formula | C$_{53}$H$_{49}$MnN$_4$Si | C$_{62}$H$_{43}$MnN$_4$Si |
| Formula weight (g/mol) | 840.99 | 943.03 |
| Temperature (K) | 98(2) | 293(2) |
| Crystal system, space group | Triclinic, $P\overline{1}$ | Triclinic, $P\overline{1}$ |
| Unit cell dimensions (Å) | | |
| $a$ = 12.482(3) | $a$ = 11.953(5) | |
| $b$ = 13.124(4) | $b$ = 13.955(6) | |
| $c$ = 14.834(3) | $c$ = 16.102(8) | |
| $\alpha$ = 75.206(17) | $\alpha$ = 101.262(8) | |
| $\beta$ = 65.422(13) | $\beta$ = 109.513(6) | |
| $\gamma$ = 85.016(16) | $\gamma$ = 93.035(7) | |
| Volume (Å$^3$) | 2136.1(9) | 2463(2) |
| $Z$ | 2 | 2 |
| Calculated density (g/cm$^3$) | 1.308 | 1.272 |
| Absorption coefficient (mm$^{-1}$) | 0.382 | 0.340 |
| F(000) | 884 | 980 |
| Crystal size (mm) | 0.35 $\times$ 0.34 $\times$ 0.05 | 0.2 $\times$ 0.2 $\times$ 0.2 |
| $\Theta$ range | 2.38 to 26.00$^\circ$ | 2.255 to 25.500$^\circ$ |
| 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 |
| [R(int) = 0.0693] | [R(int) = 0.0612] |
| Completeness to $\Theta$ | 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 $F^2$ | 1.010 | 1.042 |
| Final R indices | $R_1 = 0.0563, \quad wR_2 = 0.1257$ | $R_1 = 0.0539, \quad wR_2 = 0.1270$ |
| [I $> 2\sigma$(I)] | | |
| R indices (all data) | $R_1 = 0.0685, \quad wR_2 = 0.1352$ | $R_1 = 0.0610, \quad wR_2 = 0.1330$ |
| Largest diff. peak and hole (e·Å$^{-3}$) | 0.471 and $-0.531$ | 0.390 and $-0.437$ |

$^5$Refinement method was full-matrix least-squares on $F^2$; wavelength = 0.71073 Å. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|; \quad wR_2 = \left(\sum[w(F_o^2 - F_c^2)]^2/\sum(w(F_o^2))^2\right)^{1/2}$.}

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