Manganese and Iron PCP Pincer Complexes – The Influence of Sterics on Structure and Reactivity

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TABLE OF CONTENT

CRYSTALLOGRAPHIC DATA S2-S3
EPR DATA S3
NMR SPECTRA S4-12
### Crystallographic Data

#### Table S1. Details for the crystal structure determination of 2a, 3, 4

<table>
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<td>yellow, block</td>
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Table S2. Details for the crystal structure determination of 5b and 5c

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EPR Data

Figure S1. X-band EPR spectra of [Fe(κ³P,C,PCP⁶⁺,t-Bu)(CO)₂] (5b) (left) and [Fe(κ³P,C,PCP⁶⁺,t-Bu)(CO)₂] (5c) (right) in toluene glass at 100 K at a microwave frequency of 9.86 GHz. The red line represents a simulation with gₓ = 2.051, gᵧ = 2.027, gẑ = 2.010, Aₓ = 45.0 G, Aᵧ = 39.3 G, and Aẑ = 48.5 G (5b) and gₓ = 2.044, gᵧ = 2.034, gẑ = 1.991, Aₓ = 20.3 G, Aᵧ = 22.5 G, and Aẑ = 14.5 G (5c).
NMR spectra

**Figure S2.** $^1$H-NMR spectrum of 1a (250 MHz, C$_6$D$_6$)

**Figure S3.** $^{13}$C($^1$H) APT NMR spectrum of 1d (63 MHz, C$_6$D$_6$)
**Figure S4.** $^{13}$C{$^{1}$H} DEPT NMR spectrum of 1d (63 MHz, C$_6$D$_6$)

**Figure S5.** $^{31}$P{$^{1}$H} NMR spectrum of 1d (101 MHz, C$_6$D$_6$)
Figure S6. $^1$H NMR spectrum of 2a (400 MHz, CD$_2$Cl$_2$)

Figure S7. $^{13}$C($^1$H) NMR spectrum of 2a (101 MHz, CD$_2$Cl$_2$)
Figure S8. \(^{31}\text{P} \{^{1}\text{H}\} \) NMR spectrum of 2a (162 MHz, CD\(_2\)Cl\(_2\))

Figure S9. \(^{1}\text{H} \) NMR spectrum of 2b (400 MHz, CD\(_2\)Cl\(_2\))
Figure S10. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 2b (101 MHz, CD$_2$Cl$_2$)

Figure S11. $^{31}$P\{\textsuperscript{1}H\} NMR spectrum of 2b (162 MHz, CD$_2$Cl$_2$)
Figure S12. $^1$H NMR spectrum of 3 (600 MHz, CD$_2$Cl$_2$)

Figure S13. $^{13}$C $^1$H NMR spectrum of 3 (151 MHz, CD$_2$Cl$_2$)
Figure S14. $^{13}$C NMR spectrum of 3 (151 MHz, CD$_2$Cl$_2$)

Figure S15. section of the HSQC NMR spectrum of 3 depicting the cross-peak of the agostic C-H bond
Figure S16. $^{31}$P{$^1$H} NMR spectrum of 3 (243 MHz, CD$_2$Cl$_2$)

Figure S17. $^1$H NMR spectrum of 4 (600 MHz, C$_6$D$_6$)
Figure S18. $^{13}$C{\textsuperscript{1}H} NMR spectrum of 4 (151 MHz, C₆D₆)

Figure S19. $^{31}$P{\textsuperscript{1}H} NMR spectrum of 4 (243 MHz, C₆D₆)