Supplemental Material

Reactivity of (Triphos)FeBr$_2$(CO) towards Sodium Borohydrides

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Table S1. Crystallographic Data for 1-Br₂(CO) and 1-H(BH₄).

|                      | 1-Br₂(CO) | 1-H(BH₄) |
|----------------------|-----------|-----------|
| chemical formula     | C₃₅H₃₃Br₂FeP₃, C₃H₅O | C₃₅H₃₈BFeP₃ |
| formula weight       | 836.30    | 606.24    |
| crystal dimensions   | 0.40 x 0.15 x 0.08 | 0.200 x 0.200 x 0.050 |
| crystal system       | monoclinic | orthorhombic |
| space group          | P2(1)/n   | P 2 1 2 1 2 1 |
| a (Å)                | 12.734(3) | 10.8439(13) |
| b (Å)                | 22.641(4) | 15.045(2) |
| c (Å)                | 13.417(3) | 19.172(3) |
| α (deg)              | 90        | 90        |
| β (deg)              | 100.452(2) | 90        |
| γ (deg)              | 90        | 90        |
| V (Å³)               | 3804.3(13) | 3127.8(7) |
| Z                    | 4         | 4         |
| T (°C)               | 140(2)    | 100.2(2)  |
| ρcalc (g cm⁻³)       | 1.460     | 1.287     |
| μ (mm⁻¹)             | 2.655     | 0.657     |
| reflections collected | 41208    | 24998     |
| data/restraints/parameters | 8661/12/436 | 55070/372 |
| R₁ [I > 2σ(I)]       | 0.0423    | 0.0291    |
| wR₂ (all data)       | 0.0899    | 0.0616    |
| Goodness-of-fit      | 1.022     | 1.017     |
| Largest peak, hole (eÅ⁻³) | 0.773, -0.541 | 0.234, -0.212 |
Figure S1. The molecular structure of 1-Br₂(CO) shown at 30% displacement ellipsoids. Hydrogen atoms and co-crystallized acetone molecule are omitted for clarity.
### Table S2. Metrical parameters for 1-Br₂(CO).

| Bond/Distance | Value       | Bond/Distance | Value       | Bond/Distance | Value       |
|---------------|-------------|---------------|-------------|---------------|-------------|
| Fe1-C1        | 1.748(4)    | C4-C5         | 1.375(5)    | C20A-C21A     | 1.375(17)   |
| Fe1-P2        | 2.1906(10)  | C5-C6         | 1.385(5)    | C20B-C21B     | 1.407(13)   |
| Fe1-P1        | 2.2522(10)  | C6-C7         | 1.387(5)    | C22-C23       | 1.529(4)    |
| Fe1-P3        | 2.2697(10)  | C8-C9         | 1.390(5)    | C24-C29       | 1.388(5)    |
| Fe1-Br2       | 2.4718(7)   | C8-C13        | 1.397(5)    | C24-C25       | 1.399(4)    |
| Fe1-Br1       | 2.4871(6)   | C9-C10        | 1.383(5)    | C25-C26       | 1.383(5)    |
| P1-C8         | 1.827(3)    | C10-C11       | 1.385(5)    | C26-C27       | 1.376(6)    |
| P1-C2         | 1.832(3)    | C11-C12       | 1.378(5)    | C27-C28       | 1.374(5)    |
| P1-C14        | 1.862(3)    | C12-C13       | 1.377(5)    | C28-C29       | 1.390(5)    |
| P2-C16B       | 1.792(12)   | C14-C15       | 1.533(5)    | C30-C31       | 1.392(5)    |
| P2-C15        | 1.826(3)    | C16A-C21A     | 1.367(12)   | C30-C35       | 1.395(5)    |
| P2-C22        | 1.828(3)    | C16A-C17A     | 1.411(15)   | C31-C32       | 1.381(5)    |
| P2-C16A       | 1.891(16)   | C16B-C21B     | 1.386(10)   | C32-C33       | 1.372(6)    |
| P3-C30        | 1.827(3)    | C16B-C17B     | 1.389(10)   | C33-C34       | 1.385(6)    |
| P3-C24        | 1.828(3)    | C17A-C18A     | 1.397(15)   | C34-C35       | 1.390(5)    |
| P3-C23        | 1.846(3)    | C17B-C18B     | 1.380(10)   | C36-O2        | 1.209(5)    |
| C1-O1         | 1.145(4)    | C18A-C19A     | 1.404(17)   | C36-C39       | 1.489(7)    |
| C2-C7         | 1.386(4)    | C18B-C19B     | 1.400(12)   | C36-C38       | 1.510(7)    |
| C2-C3         | 1.397(5)    | C19A-C20A     | 1.392(14)   |               |             |
| C3-C4         | 1.388(4)    | C19B-C20B     | 1.352(14)   |               |             |
| C1-Fe1-P2     | 95.41(11)   | C16B-P2-Fe1   | 124.0(3)    |               |             |
| C1-Fe1-P1     | 92.81(10)   | C15-P2-Fe1    | 109.15(12)  |               |             |
| P2-Fe1-P1     | 83.89(3)    | C22-P2-Fe1    | 108.78(11)  |               |             |
| C1-Fe1-P3     | 95.061(10)  | C16A-P2-Fe1   | 114.4(4)    |               |             |
| P3-Fe1-P3     | 86.89(3)    | C30-P3-C24    | 100.08(14)  |               |             |
| P1-Fe1-P3     | 168.05(4)   | C30-P3-C23    | 104.98(16)  |               |             |
| C1-Fe1-Br2    | 178.63(11)  | C24-P3-C23    | 102.46(15)  |               |             |
| P2-Fe1-Br2    | 85.74(3)    | C30-P3-Fe1    | 118.76(11)  |               |             |
| P1-Fe1-Br2    | 86.55(3)    | C24-P3-Fe1    | 121.49(11)  |               |             |
| P3-Fe1-Br2    | 85.20(3)    | C23-P3-Fe1    | 106.97(10)  |               |             |
| C1-Fe1-Br1    | 86.02(11)   | O1-C1-Fe1     | 178.1(3)    |               |             |
| P2-Fe1-Br1    | 178.52(3)   | C7-C2-C3      | 118.6(3)    |               |             |
| P1-Fe1-Br1    | 95.65(3)    | C7-C2-P1      | 119.5(3)    |               |             |
| P3-Fe1-Br1    | 93.37(3)    | C3-C2-P1      | 121.7(2)    |               |             |
| Br2-Fe1-Br1   | 92.83(2)    | C4-C3-C2      | 120.1(3)    |               |             |
| C8-P1-C2      | 102.54(14)  | C5-C4-C3      | 120.5(3)    |               |             |
| C8-P1-C14     | 105.93(15)  | C4-C5-C6      | 120.1(3)    |               |             |
| C2-P1-C14     | 101.54(15)  | C5-C6-C7      | 119.5(3)    |               |             |
| C8-P1-Fe1     | 111.75(10)  | C2-C7-C6      | 121.2(3)    |               |             |
| C2-P1-Fe1     | 124.17(11)  | C9-C8-C13     | 117.9(3)    |               |             |
| C14-P1-Fe1    | 109.23(11)  | C9-C8-P1      | 122.9(3)    |               |             |
| C16B-P2-C15   | 99.4(2)     | C13-C8-P1     | 122.9(3)    |               |             |
| C16B-P2-C22   | 105.6(4)    | C10-C9-C8     | 121.4(3)    |               |             |
| C15-P2-C22    | 109.10(16)  | C9-C10-C11    | 119.8(3)    |               |             |
| C16B-P2-C16A  | 15.4(3)     | C12-C11-C10   | 119.3(3)    |               |             |
| C15-P2-C16A   | 114.7(3)    | C13-C12-C11   | 121.0(3)    |               |             |
| C22-P2-C16A   | 100.1(5)    | C12-C13-C8    | 120.6(3)    |               |             |

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Figure S2. The molecular structure of 1-H(BH₄) displayed at 30% displacement ellipsoids. Hydrogen atoms omitted for clarity.
Table S3. Metrical parameters for 1-H(BH₄).

| Bond                  | Distance | Angle     |     |
|-----------------------|----------|-----------|-----|
| Fe1-B1                | 1.026(4) | 1.409(5)  | 1.90(5) |
| Fe1-P2                | 2.082(10)| 1.374(5)  | 1.90(5) |
| Fe1-P1                | 2.174(10)| 1.382(7)  | 1.90(5) |
| Fe1-P3                | 2.182(10)| 1.390(5)  | 1.90(5) |
| Fe1-H1M               | 1.37(3)  | 1.361(7)  | 1.90(5) |
| Fe1-H1B               | 1.59(3)  | 1.409(6)  | 1.90(5) |
| Fe1-H2B               | 1.59(3)  | 1.393(5)  | 1.90(5) |
| P1-C1                 | 1.843(3) | 1.406(5)  | 1.90(5) |
| P1-C5                 | 1.844(4) | 1.398(5)  | 1.90(5) |
| P1-C1                 | 1.871(4) | 1.383(6)  | 1.90(5) |
| P2-C1                 | 1.831(3) | 1.391(6)  | 1.90(5) |
| P2-C2                 | 1.848(4) | 1.381(5)  | 1.90(5) |
| P2-C3                 | 1.850(3) | 1.3875(5) | 1.90(5) |
| P3-C29                | 1.830(3) | 1.394(5)  | 1.90(5) |
| P3-C4                 | 1.850(3) | 1.383(5)  | 1.90(5) |
| C1-C2                 | 1.532(5) | 1.381(5)  | 1.90(5) |
| C3-C4                 | 1.532(5) | 1.396(5)  | 1.90(5) |

| Bond                  | Distance | Angle     |     |
|-----------------------|----------|-----------|-----|
| B1-Fe1-P2             | 143.44(12)| 108.58(12)| 1.90(5) |
| B1-Fe1-P1             | 101.39(12)| 112.20(12)| 1.90(5) |
| P2-Fe1-P1             | 86.47(4)  | 103.03(15)| 1.90(5) |
| B1-Fe1-P3             | 98.86(12)| 103.07(16)| 1.90(5) |
| P2-Fe1-P3             | 86.80(4)  | 103.45(16)| 1.90(5) |
| P1-Fe1-P3             | 154.13(4)| 116.75(11)| 1.90(5) |
| B1-Fe1-H1M            | 135.7(13)| 121.05(12)| 1.90(5) |
| P2-Fe1-H1M            | 80.8(13)  | 107.37(12)| 1.90(5) |
| P1-Fe1-H1M            | 78.9(13)  | 110.7(2)  | 1.90(5) |
| P3-Fe1-H1M            | 75.4(13)  | 107.8(2)  | 1.90(5) |
| B1-Fe1-H1B            | 35.9(12)  | 109.4(2)  | 1.90(5) |
| P2-Fe1-H1B            | 177.9(12)| 108.6(2)  | 1.90(5) |
| P1-Fe1-H1B            | 91.8(11)  | 117.3(4)  | 1.90(5) |
| P3-Fe1-H1B            | 95.3(12)  | 124.4(3)  | 1.90(5) |
| H1M-Fe1-H1B           | 100.0(17)| 118.1(3)  | 1.90(5) |
| B1-Fe1-H2B            | 35.3(12)  | 122.3(4)  | 1.90(5) |
| P2-Fe1-H2B            | 108.12(12)| 119.8(4)  | 1.90(5) |
| P1-Fe1-H2B            | 102.8(11) | 119.7(4)  | 1.90(5) |
| P3-Fe1-H2B            | 103.1(11) | 121.0(4)  | 1.90(5) |
| H1M-Fe1-H2B           | 170.9(18)| 119.9(4)  | 1.90(5) |
| H1B-Fe1-H2B           | 71.0(16)  | 118.7(3)  | 1.90(5) |
| C11-P1-C5             | 100.18(16)| 120.9(3)  | 1.90(5) |
| C11-P1-C1             | 103.75(16)| 120.4(3)  | 1.90(5) |
| C5-P1-C1              | 104.04(18)| 120.5(3)  | 1.90(5) |
| C11-P1-Fe1            | 114.57(13)| 120.0(4)  | 1.90(5) |
| C5-P1-Fe1             | 122.36(12)| 120.1(4)  | 1.90(5) |
| C1-P1-Fe1             | 109.91(12)| 120.1(4)  | 1.90(5) |
| C17-P2-C2             | 120.00(16)| 120.6(4)  | 1.90(5) |
| C17-P2-C3             | 101.41(16)| 119.4(3)  | 1.90(5) |
| C2-P2-C3              | 108.05(16)| 120.5(3)  | 1.90(5) |
| C17-P2-Fe1            | 123.40(11)| 120.1(3)  | 1.90(5) |
Figure S3. $^1$H NMR spectrum of $1$-$\text{Br}_2$(CO) in chloroform-$d$.

Figure S4. $^{13}$C NMR spectrum of $1$-$\text{Br}_2$(CO) in chloroform-$d$. 
Figure S5. $^{31}$p NMR spectrum of $1$-$\text{Br}_2$(CO) in chloroform-\textit{d}.

Figure S6. Solid-state infrared spectrum of $1$-$\text{Br}_2$(CO) in KBr.
Figure S7. $^1$H NMR spectrum of 1-H(Br)(CO) in chloroform-$d$.

Figure S8. $^{31}$P-1H NMR spectrum of 1-H(Br)(CO) in chloroform-$d$. 
Figure S9. $^{13}$C NMR spectrum of 1-H(Br)(CO) in chloroform-$d$.

Figure S10. $^{31}$P NMR spectrum of 1-H(Br)(CO) in chloroform-$d$. 
Figure S11. Infrared spectrum of 1-H(Br)(CO) in benzene-$d_6$.

Figure S12. $^1$H NMR spectrum collected after heating 1-H(Br)(CO) at 60 °C for 20 h in chloroform-$d$. 
Figure S13. $^{1}$H NMR spectrum of 1-(CO)$_2$ in benzene-$d_6$.

Figure S14. $^{13}$C NMR spectrum of 1-(CO)$_2$ in benzene-$d_6$. 
Figure S15. $^{31}$P NMR spectrum of 1-(CO)$_2$ in benzene-$d_6$.

Figure S16. Infrared spectrum of 1-(CO)$_2$ in benzene-$d_6$. 
Figure S17. $^1$H NMR spectrum of 1-(CO)$_2$ and the putative cis-dihydride compound following 2.2 eq. NaEt$_3$BH addition to 1-Br$_2$(CO).

Figure S18. $^{31}$P NMR spectrum of 1-(CO)$_2$ and the putative cis-dihydride compound following 2.2 eq. NaEt$_3$BH addition to 1-Br$_2$(CO).
Figure S19. $^1\text{H}$ NMR spectrum of 1-H(BH$_4$) in benzene-$d_6$.

Figure S20. $^{31}\text{P}$ $^1\text{H}$ NMR spectrum of 1-H(BH$_4$) in benzene-$d_6$. 
Figure S21. $^{13}$C NMR spectrum of 1-H(BH$_4$) in benzene-$d_6$.

Figure S22. $^{31}$P NMR spectrum of 1-H(BH$_4$) in benzene-$d_6$. 
Figure S23. $^2$H NMR spectrum of 1-D(BD₄) in benzene.