Supplemental Material

Reactivity of (Triphos)FeBr₂(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	C ₃₅ H ₃₃ Br ₂ FeP ₃ , C ₃ H ₆ O	C ₃₄ H ₃₈ BFeP ₃
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 21 21 21
<i>a</i> (Å)	12.734(3)	10.8439(13)
<i>b</i> (Å)	22.641(4)	15.045(2)
<i>c</i> (Å)	13.417(3)	19.172(3)
α (deg)	90	90
β (deg)	100.452(2)	90
γ (deg)	90	90
<i>V</i> (Å ³)	3804.3(13)	3127.8(7)
<i>Z</i>	4	4
<i>T</i> (°C)	140(2)	100.(2)
ρ_{calcd} (g cm ⁻³)	1.460	1.287
μ (mm ⁻¹)	2.655	0.657
reflections collected	41208	24998
data/restraints/parameters	8661/12/436	5507/0/372
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0423	0.0291
<i>wR</i> ₂ (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)**.

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)	C15-C14-P1	112.9(2)
C1-Fe1-P1	92.81(10)	C15-P2-Fe1	109.15(12)	C14-C15-P2	110.3(2)
P2-Fe1-P1	83.89(3)	C22-P2-Fe1	108.78(11)	C21A-C16A-C17A	118.6(12)
C1-Fe1-P3	95.61(10)	C16A-P2-Fe1	114.4(4)	C21A-C16A-P2	122.5(10)
P2-Fe1-P3	86.89(3)	C30-P3-C24	100.08(14)	C17A-C16A-P2	118.6(7)
P1-Fe1-P3	168.05(4)	C30-P3-C23	104.98(16)	C21B-C16B-C17B	118.7(10)
C1-Fe1-Br2	178.63(11)	C24-P3-C23	102.46(15)	C21B-C16B-P2	117.3(7)
P2-Fe1-Br2	85.74(3)	C30-P3-Fe1	118.76(11)	C17B-C16B-P2	124.0(6)
P1-Fe1-Br2	86.55(3)	C24-P3-Fe1	121.49(11)	C18A-C17A-C16A	121.6(10)
P3-Fe1-Br2	85.20(3)	C23-P3-Fe1	106.97(10)	C18B-C17B-C16B	121.2(8)
C1-Fe1-Br1	86.02(11)	O1-C1-Fe1	178.1(3)	C17A-C18A-C19A	117.1(10)
P2-Fe1-Br1	178.52(3)	C7-C2-C3	118.6(3)	C17B-C18B-C19B	119.3(8)
P1-Fe1-Br1	95.65(3)	C7-C2-P1	119.5(3)	C20A-C19A-C18A	121.4(10)
P3-Fe1-Br1	93.37(3)	C3-C2-P1	121.7(2)	C20B-C19B-C18B	120.4(8)
Br2-Fe1-Br1	92.83(2)	C4-C3-C2	120.1(3)	C21A-C20A-C19A	119.4(10)
C8-P1-C2	102.54(14)	C5-C4-C3	120.5(3)	C19B-C20B-C21B	120.3(8)
C8-P1-C14	105.93(15)	C4-C5-C6	120.1(3)	C16A-C21A-C20A	121.7(11)
C2-P1-C14	101.54(15)	C5-C6-C7	119.5(3)	C16B-C21B-C20B	120.1(8)
C8-P1-Fe1	111.75(10)	C2-C7-C6	121.2(3)	C23-C22-P2	108.1(2)
C2-P1-Fe1	124.17(11)	C9-C8-C13	117.9(3)	C22-C23-P3	111.5(2)
C14-P1-Fe1	109.23(11)	C9-C8-P1	118.5(2)	C29-C24-C25	119.1(3)
C16B-P2-C15	99.4(2)	C13-C8-P1	122.9(3)	C29-C24-P3	121.6(3)
C16B-P2-C22	105.6(4)	C10-C9-C8	121.4(3)	C25-C24-P3	119.2(3)
C15-P2-C22	109.10(16)	C9-C10-C11	119.8(3)	C26-C25-C24	120.3(4)
C16B-P2-C16A	15.4(3)	C12-C11-C10	119.3(3)	C27-C26-C25	119.9(4)
C15-P2-C16A	114.7(3)	C13-C12-C11	121.0(3)	C28-C27-C26	120.5(3)
C22-P2-C16A	100.1(5)	C12-C13-C8	120.6(3)	C27-C28-C29	120.3(4)

C24-C29-C28	119.9(3)	C32-C31-C30	120.1(4)	C34-C35-C30	120.2(3)
C31-C30-C35	118.9(3)	C33-C32-C31	121.2(4)	O2-C36-C39	122.3(5)
C31-C30-P3	122.7(3)	C32-C33-C34	119.4(4)	O2-C36-C38	121.1(5)
C35-C30-P3	118.4(3)	C33-C34-C35	120.2(4)	C39-C36-C38	116.5(4)

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)**.

Fe1-B1	2.106(4)	C5-C10	1.395(5)	C23-C24	1.390(5)
Fe1-P2	2.1286(10)	C5-C6	1.395(5)	C23-C28	1.400(5)
Fe1-P1	2.1745(10)	C6-C7	1.374(5)	C24-C25	1.395(5)
Fe1-P3	2.1829(10)	C7-C8	1.382(7)	C25-C26	1.384(5)
Fe1-H1M	1.37(3)	C8-C9	1.361(7)	C26-C27	1.387(5)
Fe1-H1B	1.59(3)	C9-C10	1.409(6)	C27-C28	1.384(5)
Fe1-H2B	1.59(3)	C11-C12	1.393(5)	C29-C34	1.390(5)
P1-C11	1.843(3)	C11-C16	1.406(5)	C29-C30	1.390(5)
P1-C5	1.844(4)	C12-C13	1.398(5)	C30-C31	1.388(5)
P1-C1	1.871(4)	C13-C14	1.383(6)	C31-C32	1.384(5)
P2-C17	1.831(3)	C14-C15	1.391(6)	C32-C33	1.378(5)
P2-C2	1.848(4)	C15-C16	1.381(5)	C33-C34	1.385(5)
P2-C3	1.850(3)	C17-C22	1.387(5)	B1-H1B	1.24(3)
P3-C29	1.830(3)	C17-C18	1.394(5)	B1-H2B	1.22(3)
P3-C23	1.847(4)	C18-C19	1.389(5)	B1-H3B	1.12(3)
P3-C4	1.850(3)	C19-C20	1.383(5)	B1-H4B	1.15(4)
C1-C2	1.532(5)	C20-C21	1.381(5)		
C3-C4	1.532(5)	C21-C22	1.396(5)		
B1-Fe1-P2	143.44(12)	C2-P2-Fe1	108.58(12)	C19-C18-C17	120.3(3)
B1-Fe1-P1	101.39(12)	C3-P2-Fe1	112.20(12)	C20-C19-C18	119.9(3)
P2-Fe1-P1	86.47(4)	C29-P3-C23	103.03(15)	C21-C20-C19	120.3(3)
B1-Fe1-P3	98.86(12)	C29-P3-C4	103.07(16)	C20-C21-C22	119.8(3)
P2-Fe1-P3	86.80(4)	C23-P3-C4	103.45(16)	C17-C22-C21	120.2(3)
P1-Fe1-P3	154.13(4)	C29-P3-Fe1	116.75(11)	C24-C23-C28	119.0(3)
B1-Fe1-H1M	135.7(13)	C23-P3-Fe1	121.05(12)	C24-C23-P3	118.3(3)
P2-Fe1-H1M	80.8(13)	C4-P3-Fe1	107.37(12)	C28-C23-P3	122.7(3)
P1-Fe1-H1M	78.9(13)	C2-C1-P1	110.7(2)	C23-C24-C25	120.5(3)
P3-Fe1-H1M	75.4(13)	C1-C2-P2	107.8(2)	C26-C25-C24	120.0(3)
B1-Fe1-H1B	35.9(12)	C4-C3-P2	109.4(2)	C25-C26-C27	119.8(3)
P2-Fe1-H1B	177.9(12)	C3-C4-P3	108.6(2)	C28-C27-C26	120.5(4)
P1-Fe1-H1B	91.8(11)	C10-C5-C6	117.3(4)	C27-C28-C23	120.2(4)
P3-Fe1-H1B	95.3(12)	C10-C5-P1	124.4(3)	C34-C29-C30	117.7(3)
H1M-Fe1-H1B	100.0(17)	C6-C5-P1	118.1(3)	C34-C29-P3	117.9(3)
B1-Fe1-H2B	35.3(12)	C7-C6-C5	122.3(4)	C30-C29-P3	124.3(3)
P2-Fe1-H2B	108.2(12)	C6-C7-C8	119.8(4)	C31-C30-C29	121.1(3)
P1-Fe1-H2B	102.8(11)	C9-C8-C7	119.7(4)	C32-C31-C30	120.1(4)
P3-Fe1-H2B	103.1(11)	C8-C9-C10	121.0(4)	C33-C32-C31	119.5(3)
H1M-Fe1-H2B	170.9(18)	C5-C10-C9	119.9(4)	C32-C33-C34	120.1(4)
H1B-Fe1-H2B	71.0(16)	C12-C11-C16	118.7(3)	C33-C34-C29	121.5(3)
C11-P1-C5	100.18(16)	C12-C11-P1	120.9(3)	Fe1-B1-H1B	48.6(15)
C11-P1-C1	103.75(16)	C16-C11-P1	120.4(3)	Fe1-B1-H2B	48.6(15)
C5-P1-C1	104.04(18)	C11-C12-C13	120.5(3)	H1B-B1-H2B	97.(2)
C11-P1-Fe1	114.57(13)	C14-C13-C12	120.0(4)	Fe1-B1-H3B	126.8(16)
C5-P1-Fe1	122.36(12)	C13-C14-C15	120.1(4)	H1B-B1-H3B	111.(2)
C1-P1-Fe1	109.91(12)	C16-C15-C14	120.1(4)	H2B-B1-H3B	111.(2)
C17-P2-C2	102.00(16)	C15-C16-C11	120.6(4)	Fe1-B1-H4B	120.8(16)
C17-P2-C3	101.41(16)	C22-C17-C18	119.4(3)	H1B-B1-H4B	112.(2)
C2-P2-C3	108.05(16)	C22-C17-P2	120.5(3)	H2B-B1-H4B	113.(2)
C17-P2-Fe1	123.40(11)	C18-C17-P2	120.1(3)	H3B-B1-H4B	112.(2)

Figure S3. ¹H NMR spectrum of **1-Br₂(CO)** in chloroform-*d*.

Figure S4. ¹³C NMR spectrum of **1-Br₂(CO)** in chloroform-*d*.

Figure S5. ^{31}P NMR spectrum of **1-Br₂(CO)** in chloroform-*d*.

Figure S6. Solid-state infrared spectrum of **1-Br₂(CO)** in KBr.

Figure S9. ¹³C NMR spectrum of **1-H(Br)(CO)** in chloroform-*d*.

Figure S10. ³¹P 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. ¹H NMR spectrum collected after heating **1-H(Br)(CO)** at 60 °C for 20 h in chloroform-*d*.

Figure S13. ¹H NMR spectrum of **1-(CO)₂** in benzene-*d*₆.

Figure S14. ¹³C 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. ^1H NMR spectrum of **1-(CO)₂** and the putative *cis*-dihydride compound following 2.2 eq. NaEt_3BH addition to **1-Br₂(CO)**.

Figure S18. ^{31}P NMR spectrum of **1-(CO)₂** and the putative *cis*-dihydride compound following 2.2 eq. NaEt_3BH addition to **1-Br₂(CO)**.

Figure S19. ¹H NMR spectrum of **1-H(BH₄)** in benzene-*d*₆.

Figure S20. {³¹P}¹H NMR spectrum of **1-H(BH₄)** in benzene-*d*₆.

Figure S21. ^{13}C NMR spectrum of **1-H(BH₄)** in benzene-*d*₆.

Figure S22. ^{31}P NMR spectrum of **1-H(BH₄)** in benzene-*d*₆.

Figure S23. ^2H NMR spectrum of **1-D(BD₄)** in benzene.