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Fischer, Senthil, Stephan, Swift, and Young, Jr. (Supplementary Information)

Seventeen-Electron Chromium(I)tricarbonyltris(phosphine) Complexes

Supported by Tris(phosphinomethyl)phenylborates

Supplementary Information

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I. General Procedures

All operations were performed under an atmosphere of 99.5% argon further purified by passage through a column of activated Aceto Corp. catalyst R3-11 and 10 Å molecular sieves. The plumbing components of the gas purification systems were made of glass and copper. Ultra-Torr® and Swagelock® fittings were employed to provide connections between glass and copper tubing that are impermeable to air. Solutions were routinely transferred via stainless steel cannulas. Gastight syringes equipped with stainless steel three-way stopcocks and needles were used to transfer solutions when necessary. Standard Schlenk techniques were employed with double manifold vacuum lines.^{S1} Solids were handled in a glove box. Solvents were purified by standard procedures and stored under argon.

Literature procedures were employed to prepare $Cr(CO)_3(C_{10}H_8)$, $W(CO)_3(EtCN)_3$, [((3,5,-Me)C₆H₃)BP^{Ph}₃]TI, **1-3**, and **7**.^{S2-S4} Other reagents were obtained from Aldrich and used as received. Alumina (activated, neutral, ~150 mesh) and Celite were treated prior to the introduction of organometallic complexes: alumina/celite (~10 cm³) was first poured hot onto a medium porosity frit. The filter flask was then evacuated and maintained under dynamic vacuum until the powder had cooled to ambient temperature.

Solution infrared spectra were acquired on a Nicolet Magna 550 FTIR spectrometer with samples sealed in 0.1 mm gastight NaCl cells. Nujol (mineral oil) mulls for IR spectra were prepared in the glove box. NMR samples were sealed under argon into 5 mm tubes and were analyzed on a Bruker 400 MHz FT-NMR spectrometer at ambient temperature. ¹H and ¹³C chemical shifts are reported in parts per million (δ) and are given with reference to residual ¹H and ¹³C solvent references relative to TMS (C₄D₈O: δ (¹H): 1.73, 3.58; δ (¹³C): 25.37, 67.57). ³¹P chemical shifts are reported in parts per million (δ) and are given with reference to 80% H₃PO₄. ¹¹B chemical shifts are reported in parts per million (δ) and are given with reference to BF₃•OEt₂. EPR spectra were acquired on a Bruker 10" EMXPlus X-band Continuous Wave EPR spectrometer at the University of Illinois School of Chemical Sciences. Melting points (uncorrected) were determined under argon in sealed capillary tubes on a Laboratory Devices Mel-Temp apparatus. Microanalyses were carried out by ALS Environmental Services, Tucson, AZ.

References

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- S4. [((3,5,-Me)C₆H₃)BP^{Ph}₃]TI, 1-3, and 7: (a) P. J. Fischer, S. Senthil, J. T. Stephan, M. L. Swift, M. D. Storlie, E. T. Chan, M. V. Vollmer, V. G. Young, Jr. *Dalton Trans.* 2018, 47, 6166. (b) P. J. Fischer, A. B. Weberg, T. D. Bohrmann, H. Xu and V. G. Young, Jr., *Dalton Trans.*, 2015, 44, 3737. (b)

II. Synthesis Descriptions and Characterization Data

Cr(CO)₃(PhBP^{Ph}₃) (4)

A deep blue suspension of [FeCp₂][PF₆] (0.292 g, 0.882 mmol) in CH₃CN (100 mL) was added dropwise over 1 hr to a yellow solution of 1 (1.200 g, 0.882 mmol) in CH₃CN (50 mL). The reaction mixture became deep red and maroon microcrystals precipitated that were isolated by filtration, washed with CH₃CN (2 * 10 mL) and dried *in vacuo*. THF (30 mL) was added to the solid; the solution was filtered. The filtrate THF was removed *in vacuo* and pentane (30 mL) was added to the residue. The solid was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo* (0.412 g, 57%). Diffusion of pentane into a nearly saturated THF/pentane solution resulted in dark red microcrystals. Mp. 219-220 °C (dec). Found: C, 70.08; H, 4.91. C₄₈H₄₁BCrO₃P₃ requires C, 70.17; H, 5.03. IR (nujol) v_{max} (CO)/cm⁻¹ 2000 (s), 1895 (m, br), 1864 (m, sh); (THF) v_{max} (CO)/cm⁻¹ 2000 (s), 1894 (m, br); (CH₂Cl₂) v_{max} (CO)/cm⁻¹ 2001 (s), 1896 (m, br). ¹¹B NMR (128 MHz, C₄D₈O): δ -10.4 (s). ¹H NMR (400 MHz, C₄D₈O): δ 8.02 (s, br), 7.62 (m), 7.49 (s, vb), 7.38 (m), 7.11 (m). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 134.0 (s), 132.1 (s), 131.0 (s), 127.3 (s), 126.4 (s), 120.1 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.8 μ_{B} (S = ¹/₂).

$Cr(CO)_{3}(((3,5-Me)C_{6}H_{3})BP^{Ph}_{3})$ (5)

A deep blue suspension of [FeCp₂][PF₆] (0.286 g, 0.864 mmol) in CH₃CN (100 mL) was added dropwise over 1 hr to a yellow solution of **2** (1.200 g, 0.864 mmol) in CH₃CN (50 mL). The reaction mixture became deep red and maroon microcrystals precipitated that were isolated by filtration, washed with CH₃CN (3 * 10 mL) and dried *in vacuo*. THF (30 mL) was added to the solid; the solution was filtered. The filtrate THF was removed *in vacuo* and pentane (30 mL) was added to the residue. The solid was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo* (0.462 g, 63%). Diffusion of pentane into a nearly saturated THF/pentane solution resulted in dark red microcrystals. Mp. 213-214 °C (dec). Found: C, 70.37; H, 5.06. C₅₀H₄₅BCrO₃P₃ requires C, 70.68; H, 5.34. IR (nujol) v_{max} (CO)/cm⁻¹ 1998 (s), 1893 (m, br), 1861 (m, sh); (THF) v_{max} (CO)/cm⁻¹ 1999 (s), 1894 (m, br). ¹¹B NMR (128 MHz, C₄D₈O): δ -10.2 (s). ¹⁴H NMR (400 MHz, C₄D₈O): δ 7.68 (s, br), 7.62 (m), 7.48 (s, vb), 7.12 (s, br), 6.79 (s), 2.36 (s, CH₃). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 135.4 (s), 131.99 (s), 131.93 (s), 130.9 (s), 128.0 (s), 120.1 (s), 22.3 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.6 μ_{B} (S = ¹/₂).

Cr(CO)₃(((3,5-CF₃)C₆H₃)BP^{Ph}₃) (6)

A deep blue suspension of [FeCp₂][PF₆] (0.286 g, 0.864 mmol) in CH₃CN (100 mL) was added dropwise over 1 hr to a yellow solution of **3** (1.293 g, 0.864 mmol) in CH₃CN (50 mL). The reaction mixture became deep red and maroon microcrystals precipitated that were isolated by filtration, washed with CH₃CN (2 * 10 mL) and dried *in vacuo*. THF (30 mL) was added to the solid; the solution was filtered. The filtrate THF was removed *in vacuo* and pentane (3 * 10 mL) was added to the residue. The solid was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo* (0.440 g, 53%). Diffusion of pentane into a nearly saturated THF/pentane solution resulted in pale red microcrystals. Mp. 192-193 °C (dec). Found: C, 62.90; H, 4.10. C₅₀H₃₉BCrF₆O₃P₃ requires C, 62.72; H, 4.11. IR (nujol) v_{max} (CO)/cm⁻¹ 1999 (s), 1895 (m, br); (THF) v_{max} (CO)/cm⁻¹ 2002 (s), 1895 (m, br); (CH₂Cl₂) v_{max} (CO)/cm⁻¹ 2003 (s), 1896 (m, br). ¹¹B NMR (128 MHz, C₄D₈O): δ -14.4 (s). ¹⁹F{¹H} NMR (376 MHz, C₄D₈O) δ -62.9. ¹H NMR (400 MHz, C₄D₈O): δ 133.8 (s), 132.5 (s), 131.1 (s), 130.2 (s), 129.8 (s), 126.0 (q, ¹J_{CF} = 273 Hz, CF₃), 120.0 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.7 μ_{B} (S = ½).

$[Et_{4}N][Cr(CO)_{3}\{\eta^{6}-(((3,5-CH_{3})C_{6}H_{3})BP^{Ph}_{3})Cr(CO)_{3}\}] (8)$

THF (45 mL) was added to [((3,5-Me)C₆H₃)BP^{Ph}₃]TI (0.489 g, 0.533 mmol) and Cr(CO)₃(C₁₀H₈) (0.402 g, 1.52 mmol) affording a bright red solution. The solution was stirred at ambient temperature (18 hr); the resulting orange solution was transferred to [Et₄N]Br (0.117 g, 0.556 mmol) and stirred (2 hr). Filtration through alumina separated a grey solid from a red filtrate. The filtrate solvent was removed in vacuo revealing an oily orange residue. Addition of Et₂O (60 mL) and trituration afforded a pale yellow solid that was isolated by filtration, washed with Et₂O until the rinses were no longer pale red indicating removal of excess $Cr(CO)_3(C_{10}H_8)$ (4 * 10 mL) and dried *in vacuo* (.409 g, 69%). Diffusion of Et₂O into a THF solution resulted in bright yellow microcrystals. Mp. 320 °C (dec). Found: C, 65.38; H, 5.74; N, 1.31. C₆₁H₆₅BCr₂NO₆P₃ requires C, 65.66; H, 5.87; N, 1.26. IR (nujol) v_{max}(CO)/cm⁻¹ 1941 (s), 1893 (s), 1863 (s), 1833 (s), 1789 (s, sh), 1773 (s); THF v_{max} (CO)/cm⁻¹ 1942 (s), 1899 (s), 1855 (s), 1803 (s). ³¹P{¹H} (162 MHz, C₄D₈O): δ 45.1 (s). ¹¹B NMR (128 MHz, C₄D₈O): δ -14.9 (s). ¹H NMR (400 MHz, C₄D₈O): δ 7.52 (s, br, 12H, o-H, PPh₂), 6.94 (m, 18H, m/p-H, PPh₂), 5.10 (s, 2H, o-H, (3,5-CH₃)C₆H₃), 5.01 (s, 1H, p-H, (3,5-CH₃)C₆H₃), 3.24 (m, 8H, Et₄N), 2.08 (s, 6H, CH₃, (3,5-CH₃)C₆H₃), 1.26 (s, br, 12H, Et₄N), 1.11 (s, br, 6H, BCH₂). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 237.1 (s, arene-bound Cr(CO)₃), 234.6 (m, phosphinebound Cr(CO)₃), 145.7 (m, *i*-C, PPh₂), 133.3 (m, *o*-C, PPh₂), 127.6 (m, *m*-C, PPh₂), 127.4 (s, *p*-C, PPh₂), 111.1 (s, (3,5-CH₃)C₆H₃), 97.8 (s, (3,5-CH₃)C₆H₃), 93.8 (s, (3,5-CH₃)C₆H₃), 53.0 (m, Et₄N), 21.3 (s, CH₃), 18.2 (m, BCH₂), 7.6 (s, Et₄N).

$$\label{eq:eq:expansion} \begin{split} \mbox{[Et_4N][W(CO)_3 \{\eta^6\mbox{-}(((3,5\mbox{-}CH_3)C_6H_3)BP^{Ph}_3)Cr(CO)_3\}] (9) \end{split}$$

THF (60 mL) was added to W(CO)₃(CH₃CH₂CN)₃ (0.654 g, 1.51 mmol) and [Et₄N][Cr(CO)₃{ η^{6} -(((3,5-CH₃)C₆H₃)BP^{Ph}₃)] (0.738 g, 0.755 mmol). The solution was refluxed (90 min). The resulting brown mixture was filtered through alumina affording a yellow filtrate; the solvent was removed *in vacuo* until ~2 mL remained. Addition of Et₂O (40 mL) resulted in precipitation of a yellow solid that was isolated by filtration, washed with Et₂O (2 * 10 mL) and dried in vacuo (0.345 g, 37%). Diffusion of Et₂O into a THF solution resulted in bright yellow microcrystals. Mp. 320 °C (dec). Found: C, 58.64; H, 5.17; N, 1.19. C₆₁H₆₅BCrNO₆P₃W requires C, 58.72; H, 5.25; N, 1.12. IR (nujol) v_{max} (CO)/cm⁻¹ 1939 (s), 1894 (s), 1858 (s), 1831 (s), 1789 (s, sh), 1775 (s); THF v_{max} (CO)/cm⁻¹ 1941 (s), 1906 (m), 1900 (m, sh), 1852 (s), 1805 (m). ³¹P{¹H} (162 MHz, C₄D₈O): δ 45.5 (s). ¹¹B NMR (128 MHz, C₄D₈O): δ -14.9 (s). ¹⁴H NMR (400 MHz, C₄D₈O): δ 7.51 (s, br, 12H, o-H, PPh₂), 6.94 (m, 18H, *m/p*-H, PPh₂), 5.29 (s, 3H, (3,5-CH₃)C₆H₃), 3.25 (m, 8H, Et₄N), 2.31 (s, 6H, CH₃, (3,5-CH₃)C₆H₃), 1.27 (m, 12H, Et₄N), 1.08 (s, br, 6H, BCH₂). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 234.3 (m, phosphine-bound Cr(CO)₃), 215.0 (s, ¹³C-¹⁸³W satellites: 215.95, 214.06, ¹*J_{CW}* = 191 Hz, arene-bound W(CO)₃), 145.4 (m, *i*-C, PPh₂), 133.1 (m, o-C, PPh₂), 127.5 (m, *m*-C, PPh₂), 127.3 (s, *p*-C, PPh₂), 111.7 (s, (3,5-CH₃)C₆H₃), 96.3 (s, (3,5-CH₃)C₆H₃), 92.0 (s, (3,5-CH₃)C₆H₃), 52.8 (m, Et₄N), 20.9 (s, CH₃), 18.4 (m, BCH₂), 7.4 (s, Et₄N).

Cr(CO)₃{η⁶-(PhBP^{Ph}₃)Cr(CO)₃} (10)

A deep blue suspension of [FeCp₂][PF₆] (0.229 g, 0.691 mmol) in THF (75 mL) was added dropwise over 45 min to a yellow solution of **7** (0.752 g, 0.691 mmol) in THF (30 mL). The resulting red solution was filtered through Celite; the filtrate solvent was removed *in vacuo* revealing a dark purple solid. CH₃CN (30 mL) was added, and the purple solid was separated from an orange solution via filtration; the solid was washed with CH₃CN (3 * 5 mL) and dried *in vacuo*. THF (30 mL) was added to this solid, and the resulting dark red solution was filtered. The filtrate solvent was removed *in vacuo*, and pentane (30 mL) was added to the solid residue. The pale red solid was isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo*. THF (30 mL) was added to the solid residue. The pale red solid was isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo* (0.383 g, 58%). Diffusion of pentane in a nearly saturated THF/pentane solution resulted in dark red microcrystals. Mp. 206-208 °C (dec). Found: C, 63.91; H, 4.29. C₅₁H₄₁BCr₂O₆P₃ requires C, 63.97; H, 4.32. IR (nujol) v_{max} (CO)/cm⁻¹ 1994 (s), 1955 (s), 1944 (s), 1885 (s), 1865 (s), 1850 (s); THF v_{max} (CO)/cm⁻¹ 2001 (m), 1950 (s), 1870 (s). ¹¹B NMR (128 MHz, C₄D₈O): δ -16.0 (s). ¹H NMR (400 MHz, C₄D₈O): δ 7.64 (m), 7.50 (s, vb), 7.11 (m), 6.11 (s, br, *o*-H, C₆H₅ bound to zerovalent Cr(CO)₃), 5.72 (app. t, J = 6 Hz, *p*-H, C₆H₅ bound to zerovalent Cr(CO)₃), 5.54 (s, br, *m*-H, C₆H₅ bound to zerovalent Cr(CO)₃). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 237.0 (s, arene-bound Cr(CO)₃), 132.3 (s), 131.2 (s), 120.1 (s), 103.3 (s), 96.7 (s), 93.4 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.8 $\mu_{\rm B}$ (S = ½).

Cr(CO)₃{η⁶-((3,5-CH₃)BP^{Ph}₃)Cr(CO)₃} (11)

A deep blue suspension of [FeCp₂][PF₆] (0.229 g, 0.691 mmol) in THF (75 mL) was added dropwise over 45 min to a yellow solution of [Et₄N][Cr(CO)₃{ η^{6} -((3,5-CH₃)C₆H₃)BP^{Ph}₃)Cr(CO)₃}] (0.771 g, 0.691 mmol). The resulting red solution was filtered through Celite; the filtrate solvent was removed *in vacuo* revealing a dark purple solid. CH₃CN (30 mL) was added, and the purple solid was separated from an orange solution via filtration; the solid was washed with CH₃CN (3 * 5 mL) and dried *in vacuo*. THF (30 mL) was added to this solid, and the resulting dark red solution was filtered. The filtrate solvent was removed *in vacuo*, and pentane (30 mL) was added to the solid residue. The pale red solid was isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo* (0.403 g, 59%). Diffusion of pentane in a nearly saturated THF/pentane solution resulted in dark red microcrystals. Mp. 263-265 °C (dec). Found: C, 64.92; H, 4.78. C₅₃H₄₅BCr₂O₆P₃ requires C, 64.58; H, 4.60. IR (nujol) v_{max} (CO)/cm⁻¹ 2005 (s), 1944 (s), 1877 (s), 1844 (s); THF v_{max} (CO)/cm⁻¹ 2001 (m), 1945 (s), 1863 (s). ¹¹B NMR (128 MHz, C₄D₈O): δ -16.1 (s). ¹H NMR (400 MHz, C₄D₈O): δ 7.64 (s, br), 7.48 (s, vb), 7.10 (s, br), 5.67 (s, br, *o*-H, (3,5-CH₃)C₆H₃), 5.42 (s, *p*-H, (3,5-CH₃)C₆H₃), 2.27 (s, CH₃). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 236.8 (s, arene-bound Cr(CO)₃), 132.2 (s), 130.9 (s), 120.0 (s), 111.1 (s), 99.5 (s), 95.6 (s), 21.3 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.7 μ_{B} (S = ¹/₂).

W(CO)₃{η⁶-((3,5-CH₃)BP^{Ph}₃)Cr(CO)₃} (12)

A deep blue suspension of $[FeCp_2][PF_6]$ (0.200 g, 0.604 mmol) in THF (75 mL) was added dropwise over 45 min to a yellow solution of $[Et_4N][W(CO)_3{\eta^6-((3,5-CH_3)C_6H_3)BP^{Ph}_3)Cr(CO)_3}]$ (1.000 g, 0.604 mmol). The resulting deep red solution was filtered through Celite; the filtrate solvent was removed *in vacuo* revealing a dark red solid. CH₃CN (25 mL) was added, and this solid was separated from an orange solution via filtration; the solid was washed with CH₃CN (3 * 5 mL) and dried *in vacuo*. THF (30 mL) was added to this solid, and the resulting dark purple solution was filtered. The filtrate solvent was removed *in vacuo*, and pentane (30 mL) was added to the solid residue. The pale red solid was isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo* (0.418 g, 62%). Diffusion of pentane in a nearly saturated THF/pentane solution resulted in dark red microcrystals. Mp. 240-241 °C (dec). Found: C, 57.53; H, 4.29. $C_{53}H_{45}BCrO_6P_3W$ requires C, 56.96; H, 4.06. IR (nujol) $v_{max}(CO)/cm^{-1}$ 2006 (s), 1944 (s), 1878 (s), 1841 (s); THF $v_{max}(CO)/cm^{-1}$ 2001 (m), 1943 (s), 1859 (s). ¹¹B NMR (128 MHz, C₄D₈O): δ -16.6 (s). ¹H NMR (400 MHz, C₄D₈O): δ 7.64 (s, br), 7.48 (s, vb), 7.10 (s, br), 5.82 (s, br, *o*-H, (3,5-CH₃)C₆H₃), 5.71 (s, *p*-H, (3,5-CH₃)C₆H₃), 2.50 (s, CH₃). ¹³C{¹H} NMR (101 MHz, C₄D₈O): δ 215.0 (s, ¹³C-¹⁸³W satellites: 215.92, 214.05, ¹J_{CW} = 189 Hz, arene-bound W(CO)₃), 132.2 (s), 130.9 (s), 120.0 (s), 111.7 (s), 98.1 (s), 93.6 (s), 21.1 (s). μ_{eff} (C₄D₈O, method of Evans, 20 °C): 1.7 μ_{B} (S = ¹/₂).

III. Thermal Ellipsoid Drawings

Figure S1: Molecular Structure of $[PPN][Cr(CO)_3(((3,5-Me)C_6H_3)BP^{Ph}_3)]$ (2)



Figure S2: Molecular Structure of $[Et_4N][Cr(CO)_3{\eta^6-(((3,5-CH_3)C_6H_3)BP^{Ph}_3)Cr(CO)_3]}$ (8)





Figure S3: Molecular Structure of $Cr(CO)_{3}\{\eta^{6}-((3,5-CH_{3})BP^{Ph}_{3})Cr(CO)_{3}\}$ (11)

IV. X-ray Crystallographic Collection and Refinement Details; Thermal Ellipsoid Drawings

REFERENCE NUMBER: 17164z

CRYSTAL STRUCTURE REPORT

C92.50H90.08BCrNO4P5

or

 $[C_{36}H_{30}NP_2] \ [C_{50}H_{45}BCrO_3P_3] \cdot 0.5(C_5H_{12}) \cdot 0.54(C_4H_{10}O) \cdot 0.46(C_4H_8O)$

Report prepared for: Prof. P. Fischer / Macalester College

September 26, 2017



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Data collection

A crystal (approximate dimensions 0.140 x 0.100 x 0.020 mm³) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker AVENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 227 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 30 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.80 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2895 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2014/6 (Sheldrick, 2014).⁴ The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0536 and wR2 = 0.1168 (F^2 , obs. data).

Structure description

The structure is the one suggested. There is one *n*-pentane located on an inversion center and compositional disorder of a THF and diethylether in a 0.46:0.54 ratio on a general site. These solvents could be refined with restraints to a sensible result.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

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⁴ SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

Some equations of interest:

$$R_{int} = \sum |F_o^2| < F_o^2 > |/\sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$
where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S1. Crystal data and structure refinement for 17164z.

Identification code	17164z		
Empirical formula	C92.50 H90.08 B Cr N O4 P	C92.50 H90.08 B Cr N O4 P5	
Formula weight	1497.39		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 13.241(3) Å	$\alpha = 92.848(8)^{\circ}$	
	<i>b</i> = 13.693(3) Å	$\beta = 96.030(7)^{\circ}$	
	c = 21.408(4) Å	$\gamma = 92.184(8)^{\circ}$	
Volume	3851.3(13) Å ³		
Ζ	2		
Density (calculated)	1.291 Mg/m ³		
Absorption coefficient	0.307 mm ⁻¹		
F(000)	1576		
Crystal color, morphology	yellow, plate	yellow, plate	
Crystal size	0.140 x 0.100 x 0.020 mm ³		
Theta range for data collection	2.295 to 26.372°		
Index ranges	$-16 \le h \le 16, -17 \le k \le 17, -26 \le l \le 26$		
Reflections collected	75317	75317	
Independent reflections	15712 [R(int) = 0.0650]		
Observed reflections	12257	12257	
Completeness to theta = 25.242°	99.8%	99.8%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.7457 and 0.5579	0.7457 and 0.5579	
Refinement method	Full-matrix least-square	Full-matrix least-squares on F^2	
Data / restraints / parameters	15712 / 61 / 995	15712 / 61 / 995	
Goodness-of-fit on F^2	1.088	1.088	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0536, wR2 = 0.1	R1 = 0.0536, wR2 = 0.1168	
<i>R</i> indices (all data)	R1 = 0.0750, wR2 = 0.1	R1 = 0.0750, wR2 = 0.1287	
Extinction coefficient	0.0069(4)	0.0069(4)	
Largest diff. peak and hole	0.690 and -0.609 e.Å ⁻³	0.690 and -0.609 e.Å ⁻³	

REFERENCE NUMBER: 17200z

CRYSTAL STRUCTURE REPORT

$C_{48}H_{41}BCrO_3P_3\\$

Report prepared for: Prof. P. Fischer / Macalester University

September 27, 2017



Victor G. Young, Jr. X-Ray Crystallographic Laboratory Department of Chemistry University of Minnesota 207 Pleasant St. S.E. Minneapolis, MN 55455



Data collection

A crystal (approximate dimensions 0.170 x 0.160 x 0.050 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 362 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.75Å. All major sections of frames were collected with 0.80° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2989 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2014/6 (Sheldrick, 2014).⁴ The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0490 and wR2 = 0.0994 (F^2 , obs. data).

Structure description

The structure is the one suggested. The Z' = 2 and this material is twinned by a 180° rotation about *b*-axis.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ¹ APEX2, Bruker Analytical X-ray Systems, Madison, WI (2004).
- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2004).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2004).

⁴ SHELXTL 2013, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

Some equations of interest:

$$R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S2. C	rystal data	and structure	refinement	for 17200z.
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Identification code	17200z		
Empirical formula	C48H41BCrO3P3		
Formula weight	821.53		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 12.532(4) Å	$\alpha = 76.936(6)^{\circ}$	
	b = 17.887(4) Å	$\beta = 76.136(5)^{\circ}$	
	c = 19.008(6) Å	$\gamma = 89.780(5)^{\circ}$	
Volume	4024(2) Å ³		
Ζ	4		
Density (calculated)	1.356 Mg/m ³		
Absorption coefficient	0.446 mm ⁻¹	0.446 mm ⁻¹	
<i>F</i> (000)	1708	1708	
Crystal color, morphology	Purple, Plate	Purple, Plate	
Crystal size	0.170 x 0.160 x 0.050 m	0.170 x 0.160 x 0.050 mm ³	
Theta range for data collection	2.299 to 28.282°	2.299 to 28.282°	
Index ranges	$-16 \le h \le 16, -23 \le k \le 2$	$-16 \le h \le 16, -23 \le k \le 23, 0 \le l \le 25$	
Reflections collected	19846	19846	
Independent reflections	19846 [<i>R</i> (int) = ?]	19846 [<i>R</i> (int) = ?]	
Observed reflections	15742	15742	
Completeness to theta = 25.242°	99.8%	99.8%	
Absorption correction	multi-scan	multi-scan	
Max. and min. transmission	0.493516 and 0.445188	0.493516 and 0.445188	
Refinement method	Full-matrix least-square	Full-matrix least-squares on F^2	
Data / restraints / parameters	19846 / 0 / 1010	19846 / 0 / 1010	
Goodness-of-fit on F^2	1.048	1.048	
<pre>Final R indices [I>2sigma(I)]</pre>	R1 = 0.0490, wR2 = 0.09	R1 = 0.0490, wR2 = 0.0994	
<i>R</i> indices (all data)	R1 = 0.0759, wR2 = 0.1	R1 = 0.0759, wR2 = 0.1139	
Largest diff. peak and hole	0.541 and -0.498 e.Å-3	0.541 and -0.498 e.Å ⁻³	

REFERENCE NUMBER: 17199z

CRYSTAL STRUCTURE REPORT

C₅₂H₄₉BCrO_{3.50}P₃ or C₅₀H₄₅BCrO₃P₃, 0.5(C₄H₈O)

Report prepared for: Prof. P. Fischer / McCalester



Victor G. Young, Jr. X-Ray Crystallographic Laboratory Department of Chemistry University of Minnesota 207 Pleasant St. S.E. Minneapolis, MN 55455





Data collection

A crystal (approximate dimensions $0.180 \times 0.160 \times 0.140 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 445 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.75 Å. All major sections of frames were collected with 0.80° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2979 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2014/6 (Sheldrick, 2014).⁴ The space group C2/c was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0368 and wR2 = 0.0859 (F^2 , obs. data).

Structure description

The structure is the one suggested. The THF is located on a crystallographic two-fold axis.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

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⁴ SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

Some equations of interest:

$$R_{int} = \sum |F_o^2| < F_o^2 > |/\sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$
where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S3. Crystal data and structure refinement for 17199z.

Identification code	17199z	17199z	
Empirical formula	C52 H49 B Cr O3.50 P3		
Formula weight	885.63		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 18.4916(17) Å	$\alpha = 90^{\circ}$	
	<i>b</i> = 12.0782(9) Å	$\beta = 98.316(4)^{\circ}$	
	c = 40.404(3) Å	$\gamma = 90^{\circ}$	
Volume	8929.2(13) Å ³		
Ζ	8		
Density (calculated)	1.318 Mg/m ³		
Absorption coefficient	0.408 mm ⁻¹	0.408 mm ⁻¹	
<i>F</i> (000)	3704	3704	
Crystal color, morphology	purple, block		
Crystal size	0.180 x 0.160 x 0.140 mr	0.180 x 0.160 x 0.140 mm ³	
Theta range for data collection	2.189 to 28.282°		
Index ranges	$-24 \le h \le 24, -13 \le k \le 16$	$-24 \le h \le 24, -13 \le k \le 16, -52 \le l \le 53$	
Reflections collected	37511	37511	
Independent reflections	11040 [R(int) = 0.0330]	11040 [R(int) = 0.0330]	
Observed reflections	9353	9353	
Completeness to theta = 25.242°	99.6%	99.6%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.7461 and 0.6965	0.7461 and 0.6965	
Refinement method	Full-matrix least-squares	Full-matrix least-squares on F^2	
Data / restraints / parameters	11040 / 35 / 571	11040 / 35 / 571	
Goodness-of-fit on F^2	1.038	1.038	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0368, wR2 = 0.08	R1 = 0.0368, wR2 = 0.0859	
<i>R</i> indices (all data)	R1 = 0.0472, wR2 = 0.09	R1 = 0.0472, wR2 = 0.0917	
Extinction coefficient	0.00014(4)	0.00014(4)	
Largest diff. peak and hole	0.404 and -0.459 e.Å ⁻³	0.404 and -0.459 e.Å ⁻³	

REFERENCE NUMBER: 18151b

CRYSTAL STRUCTURE REPORT

 $C_{61}H_{65}BCr_2NO_6P_3$

Report prepared for: Prof. P. Fischer - Macalester University



September 25, 2018

Victor G. Young, Jr. X-Ray Crystallographic Laboratory Department of Chemistry University of Minnesota 207 Pleasant St. S.E. Minneapolis, MN 55455



Data collection

A crystal (approximate dimensions $0.210 \times 0.120 \times 0.110 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 395 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 40 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.75 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2956 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2018/3 (Sheldrick, 2014).⁴ The space group P2₁/n was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0760 and wR2 = 0.1841 (F^2 , obs. data).

Structure description

The structure is the one suggested. This is a solvate of both THF and DEE. The anion of interest is a salt with TEA. The TEA is located on inversion centers, but since it has idealized S₄ symmetry, it is statistically disordered. This means there are two TEA sites each being $\frac{1}{2}$ occupied. Appropriate restraints and constraints were used to refine the TEA cations. There were two THF and one DEE solvent molecules located in the crystal structure per asymmetric unit: please view the unit cell drawing to inspect the voids where disordered solvent was removed with PLATON/SQUEEZE. Ultimately, all solvent was removed from the model since it was poorly ordered. It is reasonable to assume the disorder of the TEA cations, each half occupied, also causes poor ordering of the solvate. PLATON/SQUEEZE found voids of 1862.5 Å³ out of 7014.6 Å³ unit cell, or 26.6%, containing 524 electrons attributed to scattering. This is a reasonable match to the solvent found during structure solution.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

Some equations of interest:

 $R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$ $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ $wR2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\right]^{1/2}$ where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$ $GooF = S = \left[\sum [w(F_o^2 - F_c^2)^2] / (n-p)\right]^{1/2}$

¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

⁴ SHELXTL 2013, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

⁵ A. L. Spek, *Acta. Cryst.* **D65**, 148-155 (2009). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Table S4. Crystal data and structure refinement for 18151b.

Identification code	18151b		
Empirical formula	C61H65BCr2NO6P3		
Formula weight	1115.86		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	$P2_1/n$		
Unit cell dimensions	a = 12.1469(16) Å	$\alpha = 90^{\circ}$	
	<i>b</i> = 17.619(2) Å	$\beta = 94.643(3)^{\circ}$	
	c = 32.885(4) Å	$\gamma = 90^{\circ}$	
Volume	7014.6(16) Å ³		
Ζ	4		
Density (calculated)	1.057 Mg/m ³		
Absorption coefficient	0.419 mm ⁻¹	0.419 mm ⁻¹	
<i>F</i> (000)	2336	2336	
Crystal color, morphology	Red, Block	Red, Block	
Crystal size	0.210 x 0.120 x 0.110 m	0.210 x 0.120 x 0.110 mm ³	
Theta range for data collection	2.193 to 28.381°		
Index ranges	$-16 \le h \le 16, -23 \le k \le 23$	$-16 \le h \le 16, -23 \le k \le 23, -43 \le l \le 33$	
Reflections collected	101735	101735	
Independent reflections	17530 [R(int) = 0.0574]	17530 [$R(int) = 0.0574$]	
Observed reflections	13712	13712	
Completeness to theta = 25.242°	99.9%	99.9%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.4330 and 0.3800	0.4330 and 0.3800	
Refinement method	Full-matrix least-squares	Full-matrix least-squares on F^2	
Data / restraints / parameters	17530 / 226 / 726	17530 / 226 / 726	
Goodness-of-fit on F^2	1.074	1.074	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0760, wR2 = 0.18	R1 = 0.0760, wR2 = 0.1841	
<i>R</i> indices (all data)	R1 = 0.0966, wR2 = 0.19	R1 = 0.0966, wR2 = 0.1973	
Largest diff. peak and hole	1.581 and -0.791 e.Å ⁻³	1.581 and -0.791 e.Å ⁻³	

REFERENCE NUMBER: 18126zzz

CRYSTAL STRUCTURE REPORT

C₅₁ H₄₁ B Cr₂ O₆ P₃

Report prepared for: Prof. P. Fischer - Macalester University

September 19, 2018



Victor G. Young, Jr. X-Ray Crystallographic Laboratory Department of Chemistry University of Minnesota 207 Pleasant St. S.E. Minneapolis, MN 55455





Data collection

A crystal (approximate dimensions 0.220 x 0.200 x 0.090 mm³) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 719 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 16 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.82 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2835 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2018/3 (Sheldrick, 2014).⁴ The space group Pbca was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0742 and wR2 = 0.1424 (F^2 , obs. data).

Structure description

The structure is the one suggested. There was disordered solvent removed from the refinement with PLATON/SQUEEZE⁵. This was likely an admixture of THF and pentane in confined voids. Two phenyl groups C22-C27 and C28-C33 were split into two fragments each in order to better model the disorder. Two other phenyls had some librational motion that was modeled well by anisotropic displacements. Appropriate restraints and constraints were included to better model these disordered fragments.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor

or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

⁴ SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2014); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

⁵ A. L. Spek, *Acta. Cryst.* **D65**, 148-155 (2009). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Some equations of interest:

$$R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S5. Crystal data and structure refinement for 18126zzz.

Identification code	18126zzz		
Empirical formula	C51H41BCr2O6P3	$C_{51}H_{41}BCr_2O_6P_3$	
Formula weight	957.56		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	Pbca		
Unit cell dimensions	a = 10.3610(13) Å	$\alpha = 90^{\circ}$	
	b = 20.185(2) Å	$\beta = 90^{\circ}$	
	c = 45.506(6) Å	$\gamma = 90^{\circ}$	
Volume	9517(2) Å ³		
Ζ	8		
Density (calculated)	1.337 Mg/m ³	1.337 Mg/m ³	
Absorption coefficient	0.606 mm ⁻¹	0.606 mm ⁻¹	
<i>F</i> (000)	3944	3944	
Crystal color, morphology	Purple, Plate	Purple, Plate	
Crystal size	0.220 x 0.200 x 0.090 m	0.220 x 0.200 x 0.090 mm ³	
Theta range for data collection	2.384 to 25.681°	2.384 to 25.681°	
Index ranges	$-12 \le h \le 12, -24 \le k \le 2$	$-12 \le h \le 12, -24 \le k \le 24, -55 \le l \le 41$	
Reflections collected	89292	89292	
Independent reflections	9037 [<i>R</i> (int) = 0.0541]	9037 [$R(int) = 0.0541$]	
Observed reflections	8198	8198	
Completeness to theta = 25.242°	99.9%	99.9%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.4311 and 0.3642	0.4311 and 0.3642	
Refinement method	Full-matrix least-squares	Full-matrix least-squares on F^2	
Data / restraints / parameters	9037 / 668 / 606	9037 / 668 / 606	
Goodness-of-fit on F^2	1.250	1.250	
<pre>Final R indices [I>2sigma(I)]</pre>	R1 = 0.0742, wR2 = 0.14	R1 = 0.0742, wR2 = 0.1424	
<i>R</i> indices (all data)	R1 = 0.0812, wR2 = 0.14	R1 = 0.0812, wR2 = 0.1459	
Largest diff. peak and hole	0.514 and -0.566 e.Å ⁻³	0.514 and -0.566 e.Å ⁻³	

REFERENCE NUMBER: 18146z

CRYSTAL STRUCTURE REPORT

 $C_{58}H_{57}BCr_2O_6P_3$

Report prepared for: Prof. P. Fischer - Macalester University

September 20, 2018



Victor G. Young, Jr. X-Ray Crystallographic Laboratory Department of Chemistry University of Minnesota 207 Pleasant St. S.E. Minneapolis, MN 55455


Data collection

A crystal (approximate dimensions 0.200 x 0.120 x 0.080 mm³) was placed onto the tip of a 0.1 mm diameter Mitegen loopand mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 357 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2956 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2018/3 (Sheldrick, 2014).⁴ The space group P -1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0467 and wR2 = 0.1092 (F^2 , obs. data).

Structure description

The structure is the one suggested. It is a 1:1 solvate of pentane.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

⁴ SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2014); G. M. Sheldrick, *Acta Cryst.* A64, 112-122 (2008).

Some equations of interest:

$$R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\right]^{1/2}$$

where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = \left[\sum [w(F_o^2 - F_c^2)^2] / (n-p)\right]^{1/2}$$

Table S6. Crystal data and structure refinement for 18146z.

Identification code	18146z	18146z	
Empirical formula	C58 H57 B Cr2 O6 P3	C58 H57 B Cr2 O6 P3	
Formula weight	1057.75		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 13.3153(17) Å	$\alpha = 75.051(2)^{\circ}$	
	b = 13.6068(17) Å	$\beta = 76.477(2)^{\circ}$	
	c = 17.191(2) Å	$\gamma = 61.345(2)^{\circ}$	
Volume	2618.2(6) Å ³		
Ζ	2		
Density (calculated)	1.342 Mg/m ³	1.342 Mg/m ³	
Absorption coefficient	0.557 mm ⁻¹	0.557 mm ⁻¹	
<i>F</i> (000)	1102	1102	
Crystal color, morphology	Red, Block	Red, Block	
Crystal size	0.200 x 0.120 x 0.080 mr	0.200 x 0.120 x 0.080 mm ³	
Theta range for data collection	2.277 to 30.602°		
Index ranges	$-19 \le h \le 18, -19 \le k \le 19$	$-19 \le h \le 18, -19 \le k \le 19, -24 \le l \le 24$	
Reflections collected	38282	38282	
Independent reflections	15924 [R(int) = 0.0425]	15924 [R(int) = 0.0425]	
Observed reflections	11704	11704	
Completeness to theta = 25.242°	99.5%	99.5%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.4330 and 0.3800	0.4330 and 0.3800	
Refinement method	Full-matrix least-squares	Full-matrix least-squares on F^2	
Data / restraints / parameters	15924 / 0 / 635	15924 / 0 / 635	
Goodness-of-fit on F^2	1.037	1.037	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0467, wR2 = 0.10	R1 = 0.0467, wR2 = 0.1092	
<i>R</i> indices (all data)	R1 = 0.0747, wR2 = 0.12	R1 = 0.0747, wR2 = 0.1263	
Largest diff. peak and hole	1.046 and -0.696 e.Å ⁻³	1.046 and -0.696 e.Å ⁻³	

REFERENCE NUMBER: 18145zz

CRYSTAL STRUCTURE REPORT

C53H45BCrO6P3W

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Data collection

A crystal (approximate dimensions 0.200 x 0.120 x 0.080 mm³) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 865 reflections. The data collection was carried out using MoK α radiation (parabolic mirrors) with a frame time of 15 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 20. The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2797 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)⁴ and refined using SHELXL-2018/3 (Sheldrick, 2014).⁴ The space group P -1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0365 and wR2 = 0.0828 (F^2 , obs. data).

Structure description

The structure is the one suggested. PLATON/SQUEEZE⁵ was used to remove the effects of disordered solvent that was impossible to model. The solvent appeared to be an admixture of both THF and pentane. This structure is not isostructural with the analogous Cr-Cr complex.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

- ¹ APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ² SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).
- ³ SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).
- ⁴ SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2014); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

⁵ A. L. Spek, *Acta. Cryst.* **D65**, 148-155 (2009). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Some equations of interest:

$$R_{int} = \sum |F_o^2| < F_o^2 > | / \sum |F_o^2|$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

where $w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$

$$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S7. Crystal data and structure refinement for 18145zz.

Identification code	18145zz	18145zz	
Empirical formula	C53H45BCrO6P3W	C53H45BCrO6P3W	
Formula weight	1117.46		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P -1		
Unit cell dimensions	a = 13.198(3) Å	$\alpha = 78.336(4)^{\circ}$	
	b = 13.261(3) Å	$\beta = 78.808(4)^{\circ}$	
	c = 17.397(4) Å	$\gamma = 61.407(4)^{\circ}$	
Volume	2601.4(10) Å ³		
Ζ	2	2	
Density (calculated)	1.427 Mg/m ³	1.427 Mg/m ³	
Absorption coefficient	2.556 mm ⁻¹	2.556 mm ⁻¹	
F(000)	1118	1118	
Crystal color, morphology	Red, Block	Red, Block	
Crystal size	0.200 x 0.120 x 0.080 m	0.200 x 0.120 x 0.080 mm ³	
Theta range for data collection	2.249 to 30.622°		
Index ranges	$-18 \le h \le 18, -18 \le k \le 1$	$-18 \le h \le 18, -18 \le k \le 18, -24 \le l \le 19$	
Reflections collected	43197	43197	
Independent reflections	15835 [$R(int) = 0.0327$]	15835 [$R(int) = 0.0327$]	
Observed reflections	13653	13653	
Completeness to theta = 25.242°	99.9%	99.9%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.3368 and 0.2701	0.3368 and 0.2701	
Refinement method	Full-matrix least-squares	Full-matrix least-squares on F^2	
Data / restraints / parameters	15835 / 0 / 588	15835 / 0 / 588	
Goodness-of-fit on F^2	1.087	1.087	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0365, wR2 = 0.08	R1 = 0.0365, wR2 = 0.0828	
<i>R</i> indices (all data)	R1 = 0.0484, wR2 = 0.09	R1 = 0.0484, wR2 = 0.0903	
Largest diff. peak and hole	2.028 and -1.928 e.Å ⁻³	2.028 and -1.928 e.Å ⁻³	

V. IR Spectra



































VI. EPR Details, Data and Spectra

Dear Paul,

Attached are the results of running the Cr(I) samples. The solutions were made in 1:1 THF/DCM and run at 77K. The instrument parameters are below. The data for the 3 compounds is virtually identical, one cannot tell the difference between the 3.

I played with the simulations. First assumed that the 3 phosphines are equivalent (C3 symmetry). The z feature with a ~1:3:3:1 is explained, but the x and y features are quite broad and no hyperfine splitting is observed. Now along the symmetry axis z the couplings should be exactly the same for c3, but in the x and y plane the couplings will not be because the projection of the Cr-P bonds point in different directions (0,120,240 deg). While this will cause some broadening, the linewidths used in the simulation for the x and y features are 40 Gauss compared to 9 Gauss for the z features. I also did the simulation assuming C2 (or equivalent Cv) symmetry (ie. rhombic symmetry). The fit is improved but I still need 48 Gauss Iw for x and 20 Gauss Iw for y. Not clear why the x and y Iw's are so large. There may be some structural homogeneity, possibly a random rhombic distortion. There also may be a homogeneous relaxation broadening due to an Orbach process involving a low lying excited state. The observation that gx ~ gy > gz ~ ge indicates the ground state is dz2 and as such non-degenerate.

These are the simulation parameters

C3:

gx,gy,gz 2.077 2.077 1.9926 Ax,Ay,Az(P1) 62 55 62 (MHz) Ax,Ay,Az(P2) 62 55 62 (MHz) Ax,Ay,Az(P3) 62 55 62 (MHz)

C2:

gx,gy,gz 2.087 2.071 1.9924 Ax,Ay,Az(P1) 81 63 69 (MHz) Ax,Ay,Az(P2) 56 65 59 (MHz) Ax,Ay,Az(P3) 56 65 59 (MHz)

The X and Y hyperfine axes are rotated by 120 and 240 degrees for P2 and P3. The lack of observable hyperfine along x and y means that measured differences in the values of Ax and Ay are approximate and have little real meaning.

Mark Nilges, PhD. Illinois EPR Research Center 506 S. Mathews St. Urbana, Il 61801

EPR Spectral Acquisition Parameters for 4

NU= 9.2920GHz DATE: 8 10 2018; TIME: 14:43 13 SCANS ; 321 A/Ds PER POINT .50 MIN. SCAN; .032 sec TC 8.00E+3 GAIN; 2.00G MODAMP; 30.00dB POWER Cr H2 77k

EPR Spectral Acquisition Parameters for 5

NU= 9.2914GHz DATE: 8 10 2018; TIME: 14:53 10 SCANS ; 321 A/Ds PER POINT .50 MIN. SCAN; .032 sec TC 8.00E+3 GAIN; 2.00G MODAMP; 30.00dB POWER (ch3)2 77K 1:1 thf dcm

EPR Spectral Acquisition Parameters for 6

NU= 9.2917GHz DATE: 8 10 2018; TIME: 15: 1 10 SCANS ; 321 A/Ds PER POINT .50 MIN. SCAN; .032 sec TC 8.00E+3 GAIN; 2.00G MODAMP; 30.00dB POWER (cf3)2 77k thf/dcm

Since the spectra of **4-6** were indistinguishable, Dr Mark Nilges provided only the plotted spectra with simulations for **4**.





VII. NMR Spectra





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