

Access to Catenated and Branched Polyphosphorus Ligands and Coordination Complexes via a Tri(pyrazolyl)phosphane

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Supporting Information

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1. Materials and Methods

General Remarks. All manipulations were performed in a Glovebox MB Unilab under an inert atmosphere of purified Argon or using Schlenk techniques. Dry, oxygen-free solvents (CH_3CN , $\text{C}_6\text{H}_5\text{F}$ (distilled from CaH_2), THF, C_6H_6 (distilled from Na/benzophenone respectively), *n*-hexane (distilled from Na)) were employed. Deuterated benzene (C_6D_6) was purchased from Sigma-Aldrich and distilled from Na. All distilled solvents were stored either over molecular sieves (4 Å; CH_3CN , C_6D_6 , $\text{C}_6\text{H}_5\text{F}$, THF) or K mirror. All reagents (Cy_2PH and $\text{Fe}_2(\text{CO})_9$) were purchased from Sigma-Aldrich. Cy_2PH was distilled prior to use. Tris-(3,5-dimethyl-1-pyrazolyl)phosphane was prepared according to the literature.^[S1] All glassware was oven-dried at 180 °C prior to use. NMR spectra were measured on a Bruker AVANCE 400 (^1H (400.03 MHz), ^{13}C (100.59 MHz), ^{31}P (161.94 MHz) at 300 K. Chemical shifts were referenced to $\delta_{\text{TMS}} = 0.00$ ppm (^1H , ^{13}C) and $\delta_{\text{H}_3\text{PO}_4(85\%)} = 0.00$ ppm (^{31}P , externally). Chemical shifts are reported in ppm. *J* values are reported in Hz. Assignments of individual resonances were done using 2-dimensional techniques (HMBC, HSQC). For compounds which give rise to a higher order spin-system in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the resolution-enhanced $^{31}\text{P}\{^1\text{H}\}$ spectrum was transferred to the software gNMR, version 5.0, by Cherwell Scientific (P. H. M. Budzelaar, *gNMR for Windows* (5.0.6.0). NMR Simulation Program, IvorySoft 2006). The full lineshape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum along with the assignment of all the peaks revealed in the resolution-enhanced spectra. The signs for the $^1J(^{31}\text{P}-^{31}\text{P})$ coupling constants were set to negative values^[S2] and all other signs of the coupling constants were obtained accordingly. The designation of the spin system was performed by convention. The furthest downfield resonance is denoted by the latest letter in the alphabet, and the furthest upfield by the earliest letter. Melting points were recorded on an electrothermal melting point apparatus in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR cell (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. Elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany.

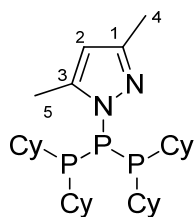
X-ray Diffraction Studies. Single crystals were coated with Paratone-N oil, mounted using a glass fiber pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected with a Nonius Kappa CCD diffractometer, equipped with rotating anode generator at 123(1) K using graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). For both compounds the Nonius software COLLECT was used for data collection.^[S3] For data reduction the Denzo-SMN program^[S4] was used and for the absorption correction the SORTAV^[S5] and Denzo^[S6] software was applied. The structure was solved by direct methods and refined by full-matrix least squares on F² (SHELXL)^[S7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model. Further details are available in table S1 (p. 9) as well as from CIF files which may be found in the CCDC data base.

Explanation for alert 901 for compound 9:

Due to the used Montel mirror we had to use a relative large X-ray beam catcher (2 mm diameter). In conjunction with large cell dimensions this leads to a relatively high amount of rejected reflections in the SCALEPACK program, mostly rejected due to their incomplete profile. This may be circumvented by increasing the distance of the detector to the crystal. However, very often this results in scaling problems. Due to the crystal size and form (plate) we obtained reasonable data only with higher generator power and longer exposure times with a small detector to crystal distance.

2. Experimental Section: Syntheses and Spectroscopic Characterization

S2.1. Preparation of 1,1,3,3-tetracyclohexyl-2-(3,5-dimethyl-1-pyrazolyl)triphosphane **6**



Dicyclohexylphosphane (1.586 g, 8.00 mmol, 2.00 eq.) was added to a solution of tris-(3,5-dimethyl-1-pyrazolyl)phosphane (1.265 g, 4.00 mmol, 1.00 eq) in CH₃CN (30 mL). The mixture was stirred over night and the formed precipitate was filtered off. The residue was suspended in CH₃CN (10 mL, 10 min) and filtered two times respectively. After removal of all volatiles from the precipitate *in vacuo* **6** was isolated in very good yields as a colourless solid (1.877 g, 91%). Mp.: 125-127 °C; Raman (30 mW, 300 K, [cm⁻¹]): 2930(100), 2890(9), 2849(62), 2826(7), 2652(5), 1441(27), 1329(5), 1296(8), 1267(8), 1027(16), 848(7), 814(13), 736(5), 697(6), 591(8), 516(6); IR (300 K, ATR, [cm⁻¹]): 2917(vs), 2846(s), 1556(w), 1442(w), 1407(w), 1322(vw), 1308(w), 1266(vw), 1180(w), 1122(w), 1018(w), 997(w), 965(w), 913(vw), 886(w), 847(w), 814(w), 780(m), 758(w), 659(vw); ¹H NMR (C₆D₆, 300 K, [ppm]): δ = 5.75 (1H, s, C2-H), 2.50-1.95 (10H, m, CH, CH₂), 2.36 (3H, s, C5-H) 2.25 (3H, s, C4-H), 1.80-1.57 (16H, m, CH₂), 1.51-1.10 (18H, m, CH₂); ¹³C NMR (C₆D₆, 300 K, [ppm]): δ = 151.5 (1C, s, C1), 146.4 (1C, d, ²J_{PC} = 19.5 Hz, C3), 106.6 (1C, s, C2), 33.9 (4C, m, CH), 32.8 (m, CH₂), 32.2 (m, CH₂), 30.9 (m, CH₂), 27.8 (m, CH₂), 14.0 (s, C4), 12.7 (d, ³J_{CP} = 15.5 Hz, C5); ³¹P{¹H} NMR (C₆D₆, 300 K, [ppm]): A₂B spin system: δ_A = 1.9 (2P), δ_B = 29.0 (1P); ¹J(P_AP_B) = -271.8 Hz; elemental analysis: calcd.: C₂₉H₅₁N₂P₃: C: 66.9, H: 9.9, N: 5.4; found: C: 66.6, H: 9.8, N: 5.3.

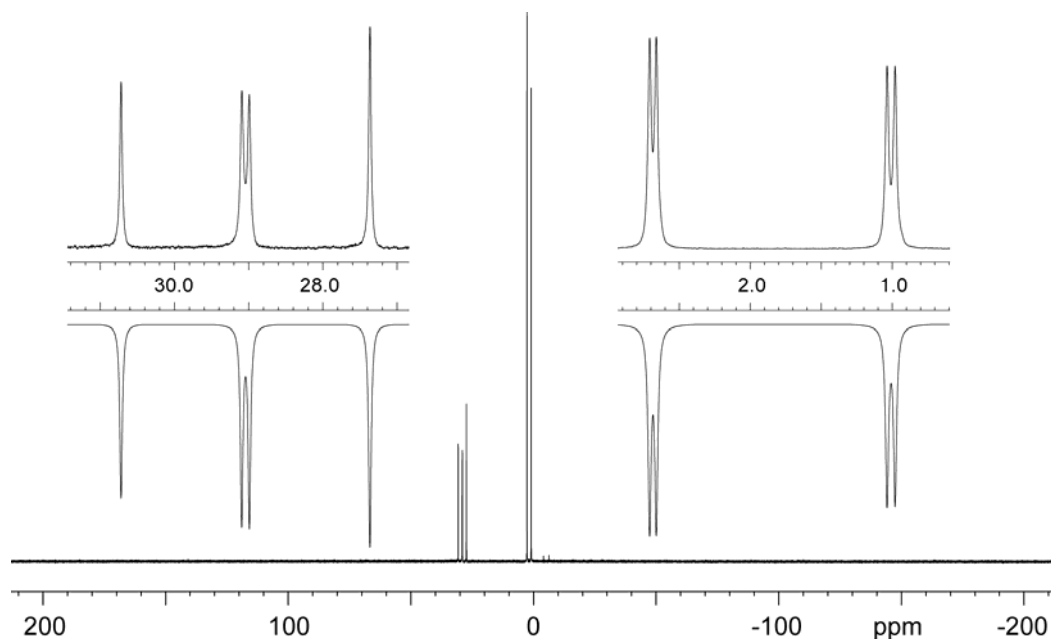
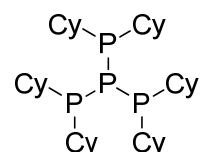


Figure S1. ³¹P{¹H} NMR spectrum of **6** (C₆D₆, 300 K; δ_A = 1.9 ppm, δ_B = 29.0 ppm; ¹J(P_AP_B) = -271.8 Hz). Expansions (inset) show the experimental (up) and fitted (down) spectra of compound **6**.

S2.2. Preparation of 1,1,3,3-cyclohexyl-2-dicyclohexylphosphanytriphosphane **1**

 Dicyclohexylphosphane (2.379 g, 12.00 mmol) was added to a solution of tris-(3,5-dimethyl-1-pyrazolyl)phosphane (0.949 g, 3.00 mmol) in CH₃CN (50 mL). The mixture was stirred for 1 week and the formed precipitate was filtered off. The residue was suspended in CH₃CN (5 mL, 10 min) and filtered three times, respectively. After removal of all volatiles from the precipitate *in vacuo* **1** was isolated in very good yields as a colourless solid (1.782 g, 95%). Mp.: 167-171 °C Raman (30 mW, 300 K, [cm⁻¹]): 2932(100), 2888(9), 2845(63), 1443(22), 1327(6), 1291(7), 1269(12), 1193(6), 1025(18), 849(7), 815(15), 694(6), 224(8), 142(8); IR (300 K, ATR, [cm⁻¹]): 2918(vs), 2845(s), 1446(m), 1339(w), 1291(vw), 1264(w), 1176(w), 1114(vw), 1025(vw), 997(w), 884(w), 849(m), 814(vw), 714(vw), 514(w), 4557(w); ¹H NMR (C₆D₆, 300 K, [ppm]): δ = 2.36-2.23 (12H, m, CH, CH₂), 2.23-2.14 (6H, m, CH₂), 1.88-1.75 (12H, m, CH₂), 1.70-1.49 (18H, m, CH₂), 1.45-1.31 (12H, m, CH₂), 1.30-1.17 (6H, m, CH₂); ¹³C NMR (C₆D₆, 300 K, [ppm]): δ = 35.6-35.1 (m, CH), 33.4-33.0 (m, CH₂), 32.2-32.0 (m, CH₂), 28.2 (d, *J*_{PC} = 11.0 Hz, CH₂), 27.8 (d, *J*_{PC} = 8.3 Hz, CH₂), 26.9 (s, CH₂); ³¹P{¹H} NMR (C₆D₆, 300 K, [ppm]): AM₃ spin system: δ_A = -108.9 (1P), δ_M = -5.2 (3P); ¹*J*(P_AP_M) = -361.9 Hz; elemental analysis: calc.: C₃₆H₆₆P₄: C: 69.4, H: 10.7; found: C: 69.0, H: 10.5.

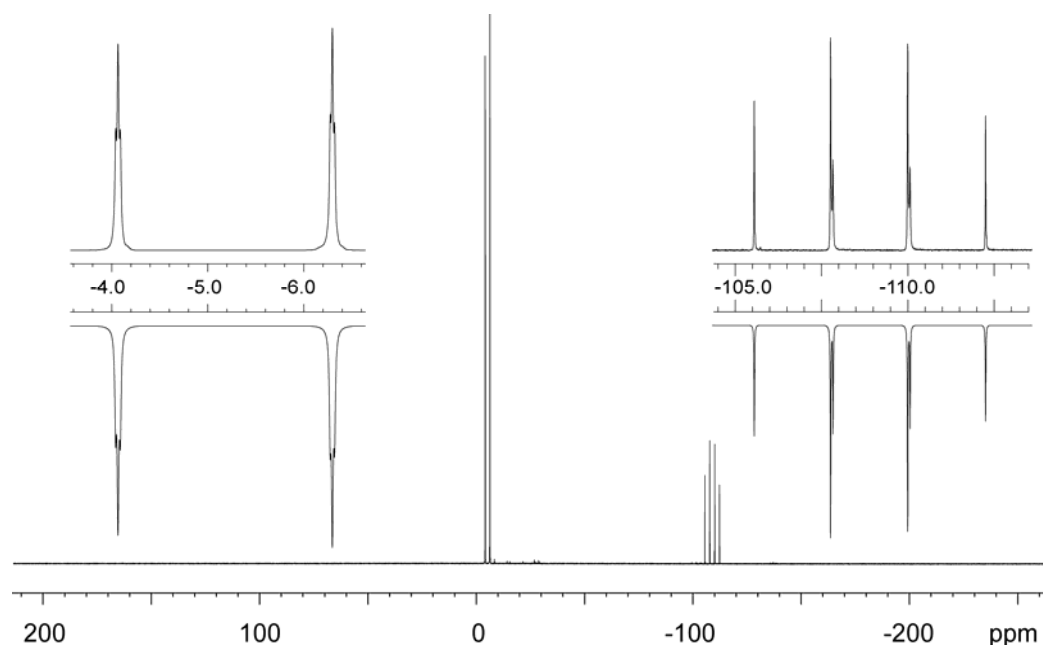
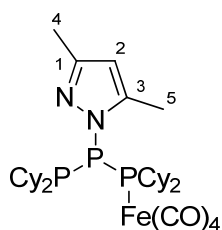


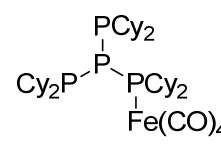
Figure S2. ³¹P{¹H} NMR spectrum of **1** (C₆D₆, 300 K; δ_A = -108.9 ppm, δ_M = -5.2 ppm; ¹*J*(P_AP_M) = -361.9 Hz). Expansions (inset) show the experimental (up) and fitted (down) spectra of compound **1**.

S2.3. 1-(1,1,3,3-tetracyclohexyl-2-(3,5-dimethyl-1-pyrazolyl)triphosphanyl)-iron(0)tetracarbonyl **9**



THF (8 mL) was added to a mixture of **6** (0.521 g, 1.00 mmol) and $\text{Fe}_2(\text{CO})_9$ (0.364 g, 1.00 mmol) at ambient temperature. The initially turbid orange mixture turned into a brown solution within 1 h. The mixture was stirred for 12 h in the dark. All volatiles were removed from the reaction mixture *in vacuo* and the residue was washed with *n*-hexane (2 x 8 mL) yielding analytically pure **9** as a beige solid (0.387 g, 56%). Crystals suitable for X-ray single crystal structure determination were obtained by slow evaporation of a benzene solution of **9**. Mp.: >160 °C (decomp.); Raman (30 mW, 300 K, $[\text{cm}^{-1}]$): 2930(100), 2880(14), 2852(64), 2046(26), 1976(39), 1948(15), 1931(13), 1919(57), 1444(35), 1327(10), 1298(10), 1272(15), 1172(7), 1045(13), 1029(26), 849(13), 816(20), 743(7), 704(13), 586(11), 486(20), 440(44), 412(11); IR (300 K, ATR, $[\text{cm}^{-1}]$): 2924(w), 2851(w), 2044(m), 1972(m), 1930(m), 1916(vs,sh), 1566(vw), 1446(w), 1326(vw), 1301(w), 1173(w), 1132(w), 1073(vw), 997(w), 964(w), 914(vw), 889(vw), 851(w), 809(w), 740(vw), 707(vw), 619(s), 550(w), 533(w), 495(w), 474(vw), 460(w), 433(vw); ^1H NMR (C_6D_6 , 300 K, [ppm]): δ = 5.92 (1H, d, $^4J_{\text{PH}}$ = 3.0 Hz, C2-H), 3.11 (1H, m, CH), 2.94 (1H, m, CH), 2.80 (1H, m, CH), 2.36 (3H, s, C5-H), 2.16 (3H, s, C4-H), 2.45-1.05 (m, CH,CH₂), 0.90-0.81 (3H, m, CH₂), 0.50 (1H, m, CH₂); ^{13}C NMR (C_6D_6 , 300 K, [ppm]): δ = 213.8 (4C, dd, J_{CP} = 15.9, 7.4 Hz, CO), 153.1 (1C, s, C1), 148.2 (1C, d, $^2J_{\text{PC}}$ = 22.4 Hz, C3), 106.9 (1C, s, C2), 40.7 (1C, ddd, J_{CP} = 8.4, 2.2, 2.2 Hz, CH), 38.5 (1C, ddd, J_{CP} = 14.7, 8.2, 6.7 Hz, CH), 34.8 (1C, d, J_{CP} = 26.0 Hz, CH), 34.3 (1C, dd, J_{CP} = 28.0, 1.8 Hz, CH₂), 33.4 (1C, dd, J_{CP} = 19.3, 9.0 Hz, CH₂), 32.8 (1C, ddd, J_{CP} = 20.3, 13.6, 6.8 Hz, CH), 31.2 (1C, s, CH₂), 31.0 (1C, dd, J_{CP} = 18.9, 9.7 Hz, CH₂), 30.5 (1C, dd, J_{CP} = 10.0, 2.0 Hz, CH₂), 29.8 (1C, J_{CP} = 6.1, 4.7 Hz, CH₂), 29.4 (2C, s, CH₂), 28.7 (1C, d, J_{CP} = 18.6 Hz, CH₂), 28.2 (1C, d, J_{CP} = 12.7 Hz, CH₂), 27.8-27.5 (2C, m, CH₂), 27.2-26.7 (3C, m, CH₂), 26.6 (1C, d, J_{CP} = 12.4, 1.9 Hz, CH₂), 26.2 (2C, s, CH₂), 26.1 (2C, s, CH₂), 13.0 (1C, s, C4), 11.9 (1C, d, $^3J_{\text{PC}}$ = 15.0 Hz, C5); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 300 K, [ppm]): AMX spin system: δ_{A} = -1.4 (1P), δ_{M} = 33.3 (1P), δ_{X} = 85.0 (1P); $^1J_{(\text{P}_{\text{A}}\text{P}_{\text{M}})}$ = -381.8 Hz, $^1J_{(\text{P}_{\text{M}}\text{P}_{\text{X}})}$ = -325.6 Hz, $^2J_{(\text{P}_{\text{A}}\text{P}_{\text{X}})}$ = 16.5 Hz; elemental analysis: calc.: $\text{C}_{33}\text{H}_{51}\text{FeN}_2\text{O}_4\text{P}_3$: C: 57.6, H: 7.5, N: 4.1; found: C: 57.6, H: 7.5, N: 3.9.

S2.4. Preparation of 1-(1,1,3,3-cyclohexyl-2-dicyclohexylphosphanyltriphosphanyl)-iron(0)tetracarbonyl **10**

 THF (10 mL) was added to a mixture of **1** (0.623 g, 1.00 mmol) and diironnonacarbonyl (0.364 g, 1.00 mmol) at ambient temperature. The initially turbid orange mixture was stirred for 12 h in the dark. The formed precipitate was filtered off, washed with THF (2 x 1 mL) and dried *in vacuo* to yield analytically pure **10** as a light-yellow solid (0.312 g, 39%). Crystals suitable for X-ray single crystal analysis were obtained by cooling (-35 °C) and slowly evaporating a fluorobenzene solution of **10** to which several drops of THF were added. Mp.: >185 °C (decomp.); Raman (30 mW, 300 K, [cm⁻¹]): 2931(100), 2890(15), 2852(76), 2040(24), 1962(54), 1925(48), 1444(29), 1340(8), 1293(9), 1269(15), 1171(7), 1046(9), 1026(19), 997(6), 849(10), 814(17), 739(6), 703(8), 499(15), 445(26); IR (300 K, ATR, [cm⁻¹]): 2920(m), 2850(w), 2039(m), 1960(m), 1920(vs,sh), 1446(w), 1326(vw), 1268(vw), 1171(w), 1046(vw), 997(w), 885(vw), 849(w), 738(vw), 705(vw), 623(s), 547(w), 512(w), 492(w), 463(vw); ¹H NMR (C₆D₆, 300 K, [ppm]): δ = 2.65 (m), 2.32-1.08 (m), 0.92-0.82 (m); ¹³C NMR (C₆D₆, 300 K, [ppm]): δ = 215.8 (m, CO), 42.8 (m, CH), 35.1 (m, CH), 34.3 (s (br), CH), 32.6 (s (br), CH₂), 32.0 (m, CH₂), 30.2 (s (br), CH₂), 28.5 (m, CH₂), 28.5 (s (br), CH₂), 28.2 (s (br), CH₂), 28.0 (m, CH₂), 27.1 (s, CH₂), 26.9 (s, CH₂); ³¹P{¹H} NMR (C₆D₆, 300 K, [ppm]): AM₂X spin system: δ_A = -70.7 (1P), δ_M = 15.4 (2P), δ_X = 97.0 (1P); ¹J(P_AP_M) = -464.9 Hz, ¹J(P_AP_X) = -345.0 Hz, ²J(P_MP_X) = 45.8 Hz; elemental analysis: calc.: C₄₀H₆₀FeO₄P₄: C: 60.8, H: 8.4; found: C: 60.8, H: 8.4.

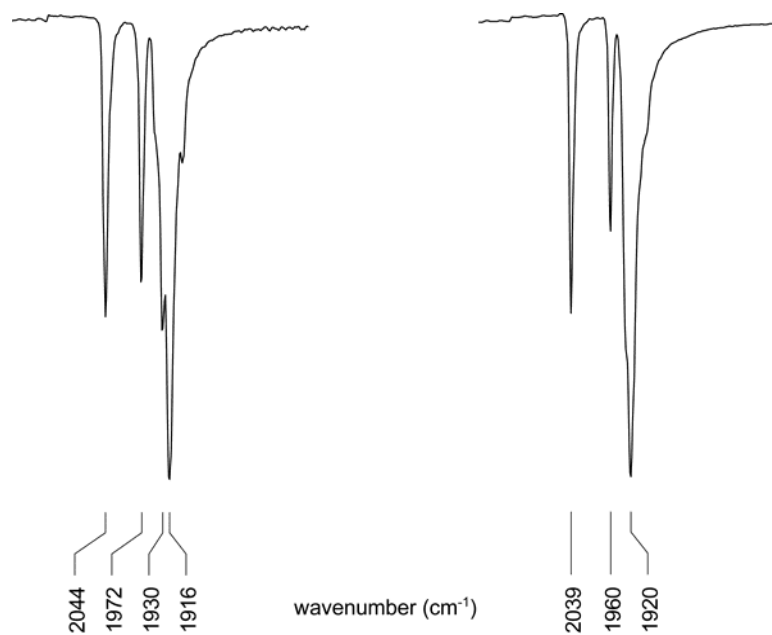


Figure S3. IR spectra of the carbonyl stretching frequencies of **9** (left) and **10** (right).

3. Crystallographic Details for compounds 9 and 10

Table S1. Crystallographic Data of **9** and **10**.

	9	10
Formula	C ₃₃ H ₅₁ FeN ₂ O ₄ P ₃	C ₄₀ H ₆₆ FeO ₄ P ₄ *C ₄ H ₈ O
MG [g mol ⁻¹]	688.52	862.76
Colour	colorless plate	yellow plate
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	11.7852(2)	12.1457(2)
<i>b</i> [Å]	29.8186(3)	34.0412(5)
<i>c</i> [Å]	20.3837(2)	11.4570(1)
α [°]	90	90.0
β [°]	97.865(1)	95.005(1)
γ [°]	90	90.0
<i>V</i> [Å ³]	7095.8(2)	4718.9(1)
<i>Z</i>	8	4
<i>T</i> [K]	153(1)	153(1)
Crystal size [mm]	0.30x0.20x0.04	0.13x0.10x0.03
ρ_c [mg m ⁻³]	1.289	1.214
<i>F</i> (000)	2928	1856
$\lambda_{\text{MoK}\alpha}$, Å	0.71073	0.71073
θ_{min} [°]	4.08	4.08
θ_{max} [°]	28.28	28.28
Index range	-15 ≤ <i>h</i> ≤ 15 -36 ≤ <i>k</i> ≤ 39 -27 ≤ <i>l</i> ≤ 26	-16 ≤ <i>h</i> ≤ 16 -45 ≤ <i>k</i> ≤ 37 -15 ≤ <i>l</i> ≤ 15
μ [mm ⁻¹]	0.598	0.495
Absorption correction	Denzo (multi-scan)	Denzo (multi-scan)
Reflection collected	46999	20296
Reflection unique	17177	11059
<i>R</i> _{int}	0.044	0.036
Reflection obs. [<i>F</i> > 2 σ (<i>F</i>)]	13877	8883
Residual density [e Å ⁻³]	0.42, -0.36	0.62, -0.83
Parameters	779	533
GooF	1.096	1.090
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0540	0.0694
<i>wR</i> ₂ (all data) ^b	0.1158	0.1721
CCDC	860158	860159

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_o| \quad ^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o)^2]} \right]^{1/2}, \text{ where } w = \left[\sigma^2(F_o^2) \right]^{-1}, P = (\max(F_o^2, 0) + 2 * F_c^2) / 3$$

4 References

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