Cis-Carbocupration of Acetylenic Phosphine Oxides and Its Application in the Stereoselective Synthesis of Polysubstituted Vinyl Phosphine Oxides

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Abstract: Bisubstituted or 1,2,2-trisubstituted vinyl phosphine oxides were prepared stereoselectively by the carbocupration of acetylenic phosphine oxides followed by hydrolysis or by reacting with other electrophiles.

Keywords: carbocupration, acetylenic phosphine oxide, polysubstituted vinyl phosphine oxides

The synthesis of stereospecifically substituted alkenes is one of the major challenges in organic synthesis, and is still being actively explored because of the fact that many biologically active compounds have the structure of substituted alkenes.[1]

We have prepared several kinds of functionalized vinyl compounds by hydrozirconation,[2a] hydrotelluration,[2b] carbomagnesiation,[3] and selenomagnesiation[4] of 1-alkynyl sulfones to afford stereodefined polysubstituted alkenes.

Unsaturated phosphorus compounds are interesting compounds owing to their synthetic utility[5] and biological activity.[6] On the other hand, vinyl phosphine oxides are useful synthetic intermediate for nucleophile addition[7] and cycloaddition reactions.[8] Also some derivatives of vinyl phosphine oxides can be used as biologically active compounds.[9] The available methodology for the stereosynthesis of substituted vinyl phosphine oxides mainly consists of hydrogen-lithium exchange reaction of vinyl phosphine oxides having no allylic hydrogen and subsequent treatment with various electrophiles,[10] using phosphonium diylides reaction with aldehydes,[11] vinyl Grignard reagent reaction with diphenylchlorophosphine and subsequently H_2O_2 oxidation,[12] olefin cross-metathesis using Grubbs and Hoveyda-type ruthenium catalysts.[13] The chemistry of organocopper(I) reagents has received a great deal of attention regarding *cis*-conjugate addition reaction with acetylenic compounds.[14] However, the Michael reaction of organocopper(I) reagents with 1-alkynyl phosphine oxides has been observed in a few cases.[15] Thus, as an extension of our study on the stereoselective synthesis of functionalized alkenes, we report herein a synthetic route for the preparation of polysubstituted vinyl phosphine oxides by the Michael addition of organocopper(I) reagents to 1-alkynyl phosphine oxides.

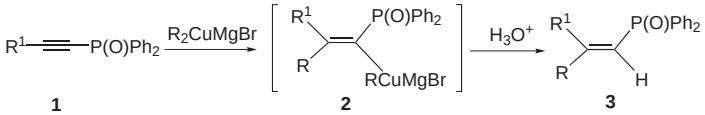
Preliminary experiments involved the treatment of 1-alkynyl phosphine oxides[16] with organocopper(I) reagents, prepared in situ from CuI and 2.0 equivalents of alkylmagnesium bromide,[17] followed by protolysis with saturated ammonium chloride solution (Scheme 1). The results are summarized in Table 1.

As indicated in Table 1, the reaction proceeds smoothly with dialkyl or diaryl cuprates at –78 °C in THF. In all cases, organocopper(I) reagents attack β-position of 1-alkynyl phosphine oxides exclusively without side reaction. The regioselectivity can be rationalized in terms of a carbanion stabilization by the phosphine oxide. It was found that a *cis*-addition happened when acetylenic phosphine oxides react with organocopper(I) reagents. The *Z*-configuration of **3c** was confirmed by NOE spectrum,

Table 1 Organcopper(I) React with 1-Alkynyl Phosphine Oxides (Electrophile = H^+)

Entry	R^1	R	Product	Yield (%)[a]	**3**[b]
1	Ph	Et	**3a**	85	only **3a**
2	$MeOCH_2$	Et	**3b**	80	only **3b**
3	$MeOCH_2$	Me	**3c**	79	only **3c**
4	C_4H_9	Ph	**3d**	82	only **3d**

[a] Isolated yield based on **1**.
[b] Other isomers were not detected in NMR studies.



Scheme 1

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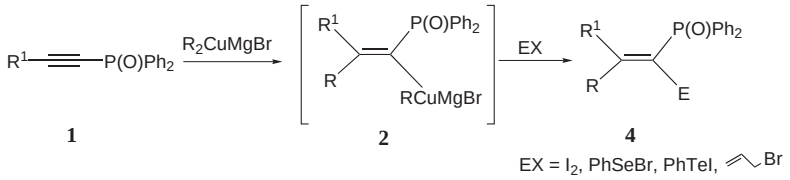

Scheme 2

which shows the correlation between the vinylic proton and the protons of methyl group, while there is no correction between the vinylic proton and the methylene group.

The vinylcopper(I) species **2** are very important intermediates because they can react with a range of electrophiles to give the α-functionalized vinyl phosphine oxides and high retention of configuration. So we further investigated the reaction of intermediate **2** with several electrophiles having transmetalation properties (I, Se, Te) (Scheme 2).[18] Results are summarized in Table 2.

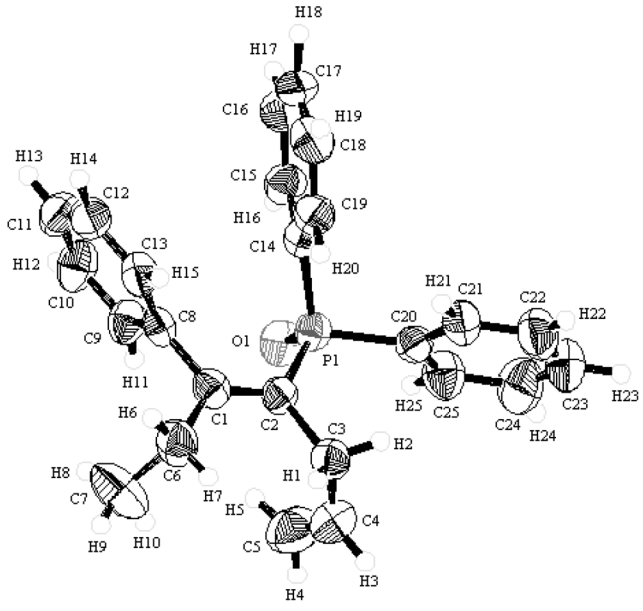

Figure 1 The molecular structure of **4g**

Table 2 Organcopper(I) React with 1-Alkynyl Phosphine Oxide (Electrophile = E^+)

Entry	R^1	R	E^+	Product	Yield (%)[a]
1	Ph	*n*-Bu	I	**4a**	85
2	$MeOCH_2$	Et	I	**4b**	79
3	Ph	Et	PhSe	**4c**	81
4	Ph	Et	PhTe	**4d**	80
5	$MeOCH_2$	Ph	PhTe	**4e**	74
6	*n*-Bu	Et		**4f**	80
7	Ph	Et		**4g**	75

[a] Isolated yield based on **1**.

α-Iodinevinylphosphine oxides **4a**, **4b** were obtained by treating the intermediate **2** with iodine. When phenylselenyl bromide or phenyltelluryl iodine was used as electrophile, α-phenylchalcogenovinyl phosphine oxides **4c**, **4d** and **4e** were formed. Allylation products **4f** and **4g** were also obtained with allyl bromide in good yields. However, attempts of acylation of the vinylcopper(I) intermediates with acetyl chloride and benzoyl chloride failed. The stereochemistry of the reaction was verified by NOESY spectra of compound **4f** and the X-ray structure of compound **4g** (Figure 1). The NOESY spectra of compound **4f** show that there is strong correlation between the allylic protons of the allyl group and the ethyl group, while no correlation was found between the allylic proton of the allyl group and the *n*-butyl group. From Figure 1, we can see that the ethyl group is *cis* oriented with respect to the allyl group. These results show that the reaction occurred in the *cis*-fashion.

In conclusion, the carbocupration of 1-alkynyl phosphine oxides and further reaction with eletrophiles provide an efficient way to synthesize polysubstituted vinyl phosphine oxides regio- and stereoselectively in a one pot process. The reactions of intermediate **2** with other electrophiles to synthesize various substituted vinyl phosphine oxides are now carried out in our laboratory.

All ^1H NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 (100 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were run on a Bruker vector 22 spectrometer. EIMS were determined with a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument. Melting points are uncorrected.

Synthesis of 3a–3d; General Procedure

CuI (142.5 mg, 0.75 mmol) was introduced into a stirred solution of Grignard reagent (1.5 mmol) in THF (3 mL) at 0 °C. After stirring for 15 min, the temperature was lowered to –78 °C. 1-Acetylenic phosphine oxides (0.5 mmol) in THF (3 mL) were added slowly and the reaction mixture was allowed to warm to –10 °C during several hours, followed by protolysis with sat. aq NH_4Cl (5 mL), then extracted with Et_2O (3 ´ 15 mL), dried with Mg_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified with flash chromatography (hexane–EtOAc, 1:1) to afford compounds **3a**–**3d**.

3a

Oil.

IR (neat): 1600, 1441, 1176 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 4 H), 7.33–7.25 (m, 6 H), 7.18–7.16 (m, 2 H), 7.06–7.04 (m, 3 H), 6.29 (d, *J* = 28.0 Hz, 1 H), 2.63 (q, *J* = 8.0 Hz, 2 H), 1.09 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.59, 139.22 (d, *J* = 7.7 Hz), 134.52 (d, *J* = 104.1 Hz), 130.95, 130.84 (d, *J* = 9.2 Hz), 128.27 (d, *J* = 11.4 Hz), 128.13, 128.06, 127.69, 118.64 (d, *J* = 105.2 Hz), 34.78 (d, *J* = 10.4 Hz), 12.54.

MS (EI): *m*/*z* (%) = 333 (100) [M^+ + 1].

Anal. Calcd for $C_{22}H_{21}OP$: C, 79.50; H, 6.37. Found: C, 79.62; H, 6.30.

3b
Oil.

IR (neat): 1580, 1445, 1170 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 4 H), 7.49–7.43 (m, 6 H), 6.05 (d, *J* = 36 Hz, 1 H), 4.40 (s, 2 H), 3.14 (s, 3 H), 2.38 (q, *J* = 8.0 Hz, 2 H), 1.12 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 134.80 (d, *J* = 104.2 Hz), 131.40 (d, *J* = 2.4 Hz), 130.60 (d, *J* = 9.5 Hz), 128.60 (d, *J* = 12.0 Hz), 119.70 (d, *J* = 101.5 Hz), 72.5 (d, *J* = 7.6 Hz), 51.3, 35.2 (d, *J* = 10.3 Hz), 12.63.

MS (EI): *m*/*z* (%) = 301 (100) [M^+ + 1].

Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.83; H, 7.13.

3c
Oil.

IR (neat): 1590, 1441, 1176 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 4 H), 7.44–7.40 (m, 6 H), 6.00 (d, *J* = 24.36 Hz, 1 H), 4.34 (s, 2 H), 3.11 (s, 3 H), 2.00 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.03, 134.95 (d, *J* = 104.1 Hz), 131.54 (d, *J* = 2.6 Hz), 130.86 (d, *J* = 9.7 Hz), 128.54 (d, *J* = 11.9 Hz), 119.49 (d, *J* = 101.7 Hz), 71.82 (d, *J* = 7.8 Hz), 51.15, 23.50 (d, *J* = 16.8 Hz).

MS (EI): *m*/*z* (%) = 287 (100) [M^+ + 1].

Anal. Calcd for $C_{17}H_{19}O_2P$: C, 71.32; H, 6.69. Found: C, 71.41; H, 6.58.

3d
Solid; mp 108–110 °C.

IR (KBr): 1599, 1440, 1176 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.65 (m, 4 H), 7.37–7.32 (m, 6 H), 7.13–7.08 (m, 5 H), 5.98 (d, *J* = 29 Hz, 1 H), 2.92 (t, *J* = 7.6 Hz, 2 H), 1.38–1.36 (m, 4 H), 0.86 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.95 (d, *J* = 2.9 Hz), 141.66 (d, *J* = 17.3 Hz), 135.19 (d, *J* = 103.9 Hz), 131.51 (d, *J* = 3.0 Hz), 131.05 (d, *J* = 9.2 Hz), 128.95, 128.63 (d, *J* = 12.0 Hz), 128.61, 126.54, 119.15 (d, *J* = 104.3 Hz), 32.66 (d, *J* = 5.8 Hz), 30.77, 22.68, 13.80.

MS (EI): *m*/*z* (%) = 361 (100) [M^+ + 1].

Anal. Calcd for $C_{24}H_{25}OP$: C, 79.98; H, 6.99. Found: C, 79.86; H, 7.01.

Synthesis of 4a–4g; General Procedure
CuI (142.5 mg, 0.75 mmol) was introduced into a stirred solution of Grignard reagent (1.5 mmol) in THF (3 mL) at 0 °C. After stirring for 15 min, the temperature was lowered to –78 °C. 1-Acetylenic phosphine oxides (0.5 mmol) in THF (3 mL) were added slowly and the reaction mixture was allowed to warm to –10 °C during several hours. Then the reaction was again cooled to –78 °C and several electrophiles {in the cases of **4a**, **4b**, iodine (0.5 mmol, 127 mg) in THF (3 mL); in the case of **4c**, phenyl selenyl bromide (1 mmol, 236 mg) in THF (3 mL); in case of **4d**, **4e**, phenyltelluryl iodine [1 mmol; prepared by reaction of diphenyl ditelluride (0.5 mmol, 204 mg) with iodine (0.5 mmol, 127 mg) in THF (3 mL) for 1 h at r.t.]; in the case of **4f**, **4g**, ally bromide (1 mmol, 121 mg) in THF (2 mL)} were added dropwise. The reaction mixtures were allowed to warm to r.t. and quenched with aq NH_4Cl (5 mL), then extracted with Et_2O (3 × 15 mL), and dried with Mg_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified with flash chromatography (hexane–EtOAc, 1:1) to afford compounds **4a**–**4g**.

4a
Oil.

IR (neat): 1603, 1448, 1183 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.65 (m, 4 H), 7.37–7.32 (m, 6 H), 7.13–7.08 (m, 5 H), 2.92 (t, *J* = 8 Hz, 2 H), 1.38–1.36 (m, 4 H), 0.86 (t, *J* = 8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.79 (d, *J* = 5.7 Hz), 139.25 (d, *J* = 2.7 Hz), 132.37 (d, *J* = 108.5 Hz), 131.96 (d, *J* = 9.3 Hz), 131.30 (d, *J* = 2.7 Hz), 128.22 (d, *J* = 12.3 Hz), 128.04, 127.95, 127.72, 97.70 (d, *J* = 90 Hz), 49.27 (d, *J* = 9.1 Hz), 28.85, 22.61, 13. 9.

MS (EI): *m*/*z* (%) = 487 (100) [M^+ + 1].

Anal. Calcd for $C_{24}H_{24}IOP$: C, 59.27; H, 4.97. Found: C, 59.35; H, 4.82.

4b
Oil.

IR (neat): 1605, 1450, 1176 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.68 (m, 4 H), 7.47–7.43 (m, 6 H), 4.37 (s, 2 H), 3.12 (s, 3 H), 2.35 (q, *J* = 8.0 Hz, 2 H), 1.18 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.88 (d, *J* = 5.4 Hz), 132.82 (d, *J* = 108.9 Hz), 132.46 (d, *J* = 9.3 Hz), 132.12 (d, *J* = 2.9 Hz), 128.38 (d, *J* = 12.8 Hz), 95.42 (d, *J* = 88.7), 70.41 (d, *J* = 6.6 Hz), 58.15, 36.35 (d, *J* = 9.6 Hz), 11.53.

Anal. Calcd for $C_{18}H_{20}IO_2P$: C, 50.72; H, 4.73; Found: C, 50.69; H, 4.82.

4c
Oil.

IR (neat): 1586, 1441, 1173 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.90 (m, 4 H), 7.50–7.47 (m, 3 H), 7.45–7.40 (m, 3 H), 7.14–7.10 (m, 3 H), 7.05–7.00 (m, 3 H), 6.98–6.94 (m, 2 H), 6.92–6.85 (m, 2 H), 2.46 (q, *J* = 8.0 Hz, 2 H), 0.95 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.40 (d, *J* = 4.8 Hz), 143.40 (d, *J* = 7.8 Hz), 138.5, 133.60 (d, *J* = 106.1 Hz), 132.10 (d, *J* = 9.2 Hz), 131.48 (d, *J* = 2.6 Hz), 130.5, 129.34 (d, *J* = 11.8 Hz), 128.80, 127.94, 127.83, 127.20, 126.16, 119.89 (d, *J* = 88.4 Hz), 32.79 (d, *J* = 10.0 Hz), 12.53.

MS (EI): *m*/*z* (%) = 488 (100) [M^+ + 1].

Anal. Calcd for $C_{28}H_{25}OPSe$: C, 68.99; H, 5.17. Found: C, 68.89; H, 5.28.

4d
Oil.

IR (neat): 1631, 1445, 1176 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.90 (m, 4 H), 7.80–7.62 (m, 3 H), 7.56–7.38 (m, 3 H), 7.29–7.15 (m, 3 H), 7.10–7.00 (m, 3 H), 6.96–6.92 (m, 2 H), 6.90–6.85 (m, 2 H), 2.58 (q, *J* = 8.0 Hz, 2 H), 0.97 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.15 (d, *J* = 4.7 Hz), 139.82 (d, *J* = 7.8 Hz), 137.6, 134.99 (d, *J* = 104.6 Hz), 131.12 (d, *J* = 8.9 Hz),

130.70 (d, *J* = 3.7 Hz), 129.47, 128.06 (d, *J* = 12.0 Hz), 127.96, 127.82, 127.73, 126.69, 118.54, 115.06 (d, *J* = 83.7 Hz), 41.98 (d, *J* = 12.0 Hz), 11.57.

MS (EI): *m/z* (%) = 537 (100) [M^+ + 1].

Anal. Calcd for $C_{28}H_{25}OPTe$: C, 62.73; H, 4.70. Found: C, 62.82; H, 4.56.

4e
Oil.

IR (neat): 1600, 1435, 1172 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 4 H), 7.52–7.47 (m, 3 H), 7.46–7.40 (m, 3 H), 7.14–7.12 (m, 3 H), 7.05–7.03 (m, 3 H), 6.98–6.96 (m, 2 H), 6.90–6.87 (m, 2 H), 4.53 (s, 2 H), 2.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.40 (d, *J* = 4.8 Hz), 139.37 (d, *J* = 8.0 Hz), 134.40 (d, *J* = 105.4 Hz), 131.77 (d, *J* = 2.0 Hz), 131.09 (d, *J* = 9.0 Hz), 129.41, 127.85, 127.67, 128.80, 127.64 (d, *J* = 11.8 Hz), 126.05, 125.67, 125.13, 118.04 (d, *J* = 88.4 Hz), 69.49 (d, *J* = 7.4 Hz), 58.13.

MS (EI): *m/z* (%) = 555 (100) [M^+ + 1].

Anal. Calcd for $C_{28}H_{25}O_2PTe$: C, 60.92; H, 4.56. Found: C, 60.86; H, 4.63.

4f
Oil.

IR (neat): 1580, 1420, 1180 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H), 7.50–7.39 (m, 6 H), 5.48–5.44 (m, 1 H), 4.84 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 2 H), 2.88 (q, *J* = 7.6 Hz, 2 H), 2.47 (t, *J* = 8.0 Hz, 2 H), 2.27 (q, *J* = 7.6 Hz, 3 H), 1.40–1.31 (m, 4 H), 1.12 (t, *J* = 7.3 Hz, 2 H), 0.74 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.90 (d, *J* = 8.2 Hz), 135.17, 134.49 (d, *J* = 99.0 Hz), 131.77 (d, *J* = 9.1 Hz), 131.18 (d, *J* = 2.2 Hz), 128.11 (d, *J* = 12.1 Hz), 123.09 (d, *J* = 107.7 Hz), 115.74, 34.25 (d, *J* = 7.8 Hz), 34.13, 26.12 (d, *J* = 13.4 Hz), 22.89, 13.77, 12.76.

MS (EI): *m/z* (%) = 353 (100) [M^+ + 1].

Anal. Calcd for $C_{23}H_{29}OP$: C, 78.38; H, 8.29. Found: C, 78.46; H, 8.17.

4g
Solid: mp 116–118 °C.

IR (KBr): 1600, 1425, 1165 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.45 (m, 4 H), 7.27–7.7.18 (m, 6 H), 6.94–6.88 (m, 5 H), 5.67–5.63 (m, 1 H), 4.99–4.93 (m, 2 H), 3.10 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 2 H), 2.50 (q, *J* = 8.0 Hz, 2 H), 0.95 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.65 (d, *J* = 8.2 Hz), 140.07 (d, *J* = 8.4 Hz), 136.53 (d, *J* = 1.6 Hz), 134.00 (d, *J* = 101.2 Hz), 131.45 (d, *J* = 10.2 Hz), 130.67 (d, *J* = 2.8 Hz), 129.17, 129.16, 127.80 (d, *J* = 11.8 Hz), 127.1, 127.00, 115.97, 34.55 (d, *J* = 13.1 Hz), 30.45 (d, *J* = 12.5 Hz), 12.05.

MS (EI): *m/z* (%) = 373 (100) [M^+ + 1].

Anal. Calcd for $C_{25}H_{25}OP$: C, 80.62; H, 6.77. Found: C, 80.50; H, 6.82.

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(19) **Crystal Data for 4g:** $C_{25}H_{25}OP$, MW = 372.45, monoclinic, space group, $P2_1/n$, a = 19.002(4), b = 6.305(2), c = 18.514(6) Å, β = 110.66(2)°, V = 2075(1) $Å^3$, T = 293K, *Z* = 4, D_c = 1.92 $g \cdot cm^{-1}$, μ = 1.44 mm^{-1}, λ = 0.71069 Å, F(000) = 792.00, independent reflections (R_{int} = 0.000), 8478 reflections collected; refinement method, full-matrix least-squares refinement on F^2; goodness-of-fit on F^2 = 0.223; Final *R* indices [$I > 2\sigma(I)$] *R*1 = 0.050, *wR*2 = 0.094.