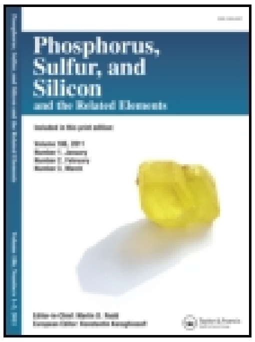

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Synthesis of phosphorus- and sulfur-stabilized carbone $(Me)Ph_2P{\rightarrow}C{\leftarrow}SPh_2(=NMe)$

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ABSTRACT

Iminosulfane(phosphane)carbon(0) (iSPC) [$(Me)Ph_2P{\rightarrow}C{\leftarrow}SPh_2(=NMe)$: **1**] is generated by the deprotonation of corresponding cationic salt **1·H**, which is obtained from the reaction of iminosulfonium methylide with Ph_2PCl and subsequent *P*-methylation. Density functional theory calculations reveal that the electronic structure of **1** has two lone pairs of electrons at the carbon center. First and second proton affinity values are theoretically calculated to be 287.2 and 187.0 kcal mol^{-1}, respectively. The highest occupied molecular orbital (HOMO) energy level of **1** is higher energy than that of bis(iminosulfane)carbon(0) (BiSC: [$(MeN=)Ph_2S{\rightarrow}C{\leftarrow}SPh_2(=NMe)$]). The reactivities of these lone pairs of electrons are demonstrated by the *C*-diaurated complex.

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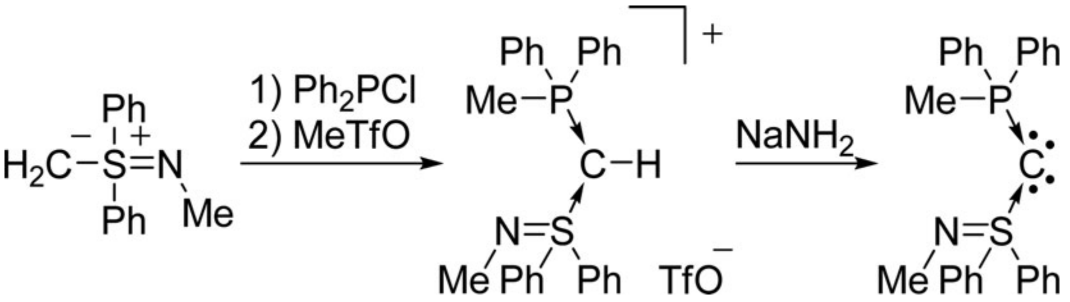
GRAPHICAL ABSTRACT



Introduction

Carbones consist of two strong electron-donating ligands, such as phosphanes in carbodiphosphorane (termed as “bis(phosphane)carbon(0) (BPC: **A**)” in our study) coordinated to the central zero-valent carbon atom, which maintains its four valence electrons in two orthogonal lone pair orbitals. Therefore, it is also described as a carbon complex (Figure 1).[1–4]

Recently, we reported the syntheses and reactivities of two-chalcogen stabilized carbones (bis(iminosulfane)carbon(0) (BiSC: **B**), iminosulfane(sulfane)carbon(0) (iSSC: **C**), and iminosulfane(selenane)carbon(0) (iSSeC: **D**)), that are four-electron donors.[5] Furthermore, we reported the syntheses of phosphorus- and sulfur-stabilized carbones (iminosulfane(phosphane)carbon(0) (iSPC: **E–G**)) bearing triaryl phosphane ligand.[6] Among them, **G** is the first thermally and moisture stable carbone stabilized by phosphorus and sulfur ligand. In these work we revealed that the electron-donating ability of central carbon in carbones can be tuned by the replacement of the ligand.

These iSPC derivatives **E–G** are synthesized by the reaction of iminosulfonium salt with corresponding triarylphosphonium ylide.[6] However, the synthetic strategies of iSPC for further structural modification remained limited by the fact that the synthetic equivalent of iminosulfonium ligand is electrophilic iminosulfonium salt $[FPh_2SNMe]BF_4$. In our previous work, we have reported that the reaction of iminosulfonium ylide **4** with carbonyl compounds affords the corresponding stable iminosulfonium ylide.[7] These results prompted us to examine the reaction of **4** with electrophilic phosphine chloride and subsequent *P*-methylation which might lead to the formation of protonated salt of iSPC **1**. We believe that an improvement in the synthetic methods and structural diversity of iSPCs might extend their utility into the realm of organometallic chemistry and catalysis. Here we report the development of a new synthetic protocol for the preparation of iSPC **1** with the alkyl substituted phosphine ligand using nucleophilic iminosulfonium methylide, and the synthesis of its *C*-diaurated complex **2** in order to clarify its four-electron donor ability. We also describe the comparison of **1** to previously reported **A**–**G**.

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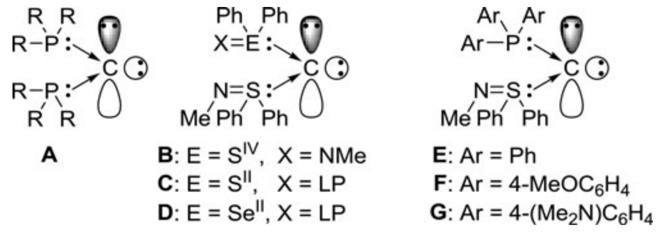


Figure 1. Molecular structures of **A–G**.

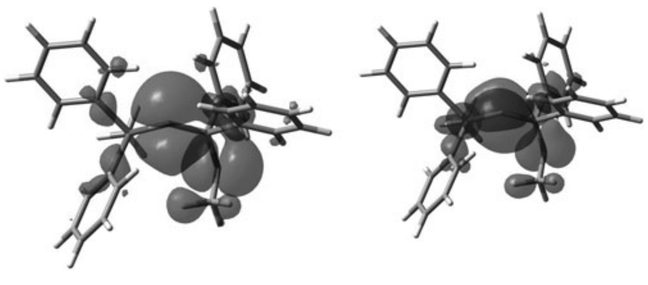


Figure 2. HOMO (left) and HOMO-1 (right) of iSPC **1**.

Results and discussion

According to our previous reports, the iminosulfonium salt **3** was synthesized by the reaction of methyldiphenyl-λ^6-sulfanenitrile with MeTfO in dichloromethane at −20°C.[7] The reaction of iminosulfonium ylide **4** with Ph_2PCl and subsequent addition of MeOTf affords the corresponding monoprotonated salt **1·H** in 35% yield (Scheme 1). The formation of **1·H** was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and X-ray crystallographic analysis.[8] iSPC **1** is cleanly generated by deprotonation of **1·H** with sodium amide or potassium hexamethyldisilazide in THF or C_6D_6. **1** is rapidly hydrolyzed to phosphine oxide **5** and sulfimide **6** under air in the solution (Scheme 1). In addition, passing **1·H** through an ion-exchange resin column (IRA-410, OH^- form) affords the hydrolyzed products. We assumed that **1** is hydrolyzed by the attack at the cationic phosphorus center by H_2O or OH^-.

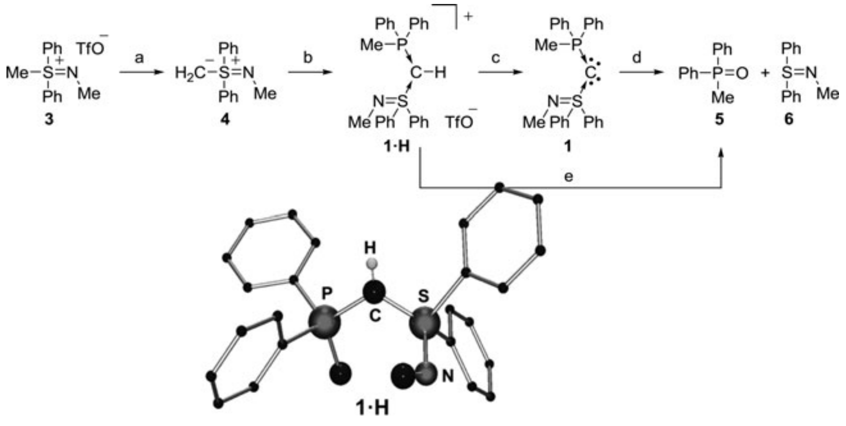
In the ^{13}C NMR spectra, the central carbon atom of **1** appears as a doublet (21.7 ppm, $^1J_{PC} = 37$ Hz), which is shifted to a lower field compared with the cationic salt (**1·H**: 12.8 ppm, $^1J_{PC} = 62$ Hz), while the signal is slightly shifted to a higher field compared with the iSPCs (**E**: 23.1 ppm, $^1J_{PC} = 62$ Hz; **F**: 23.0 ppm, $^1J_{PC} = 58$ Hz; **G**: 23.6 ppm, $^1J_{PC} = 68$ Hz).[6] These values suggest the carbone character of **1**.[9] In the ^{31}P NMR spectra, the signal of **1** (−8.29 ppm) is significantly shifted to a higher field than that of cationic salt **1·H** (12.5 ppm), iSPC (**E**: −2.64 ppm; **F**: −3.51 ppm; **G**: −1.39 ppm) and BPC (−2.14 ppm).[6,10] Unfortunately, all attempts to grow X-ray quality single crystals for diffraction analysis of **1** were unsuccessful.

To gain insight into the electronic structures of **1**, density functional theory (DFT) calculations at the B3PW91/6–311G(d,p) level are performed (Figure 2).[11,12] Inspection of the frontier orbitals reveals that the central carbon atom of **1** has two lone pair orbitals in the highest occupied molecular orbital (HOMO: $n\pi_C$; HOMO−1: $n\sigma_C$; Figure 2). Natural bond orbital (NBO) analyses indicate that $n\sigma_C$ has an s character (33%), indicating a hybridization close to sp[2], whereas the $n\pi_C$ lone pair has 100% p character. The central carbon atom of **1** bears a large negative charge (−1.38 e), which is similar to that of BPC (**A**: −1.55 e), BChCs (**B**: −1.24 e; **C**: −1.20 e; **D**: −1.25 e), and iSPCs (**E**–**G**: −1.38 e).[1,5b,6] The Wiberg bond index value of iSPC for the P→C (1.25) is lower than that of S→C (1.31), which is similar to the trend observed in iSPCs (P→C: **E**: 1.26, **F**: 1.24, **G**: 1.22; S→C: **E**: 1.30, **F**: 1.31, **G**: 1.34).[6]

To verify the carbone character, we calculated the first and second proton affinities (PA(1) and PA(2)) of **1** and compared them with the theoretically predicted values for the PAs of carbones **A**–**G** (Table 1). The theoretically predicted PA(1) of **1** is quite high, suggesting their strong basic character. The calculations predict that iSPC **1** has a higher PAs than BiSC **B**, whereas

Table 1. Calculated energy levels of the HOMO, HOMO–1 and proton affinities (PAs) of **1** and **A**–**G** at B3PW91/6–311G(d,p).

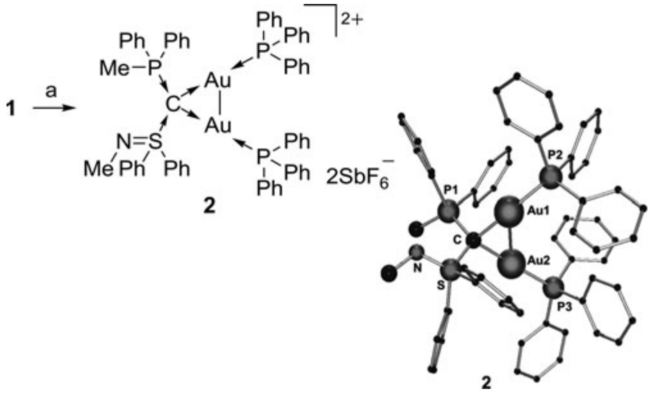
	HOMO (eV)	HOMO-1 (eV)	PA(1) (kcal mol^{-1})	PA(2) (kcal mol^{-1})
1	−5.05	−5.29	287.2	187.0
A[6]	−4.82	−5.01	294.8	197.7
B[5b]	−5.26	−5.56	278.8	182.2
C[5b]	−5.08	−5.32	288.0	184.4
D[5b]	−5.09	−5.36	287.1	187.0
E[6]	−5.05	−5.27	286.8	189.6
F[6]	−4.86	−5.07	292.7	198.4
G[6]	−4.58	−4.73	301.6	207.8



Scheme 1. Synthesis of **1** and molecular structure of **1·H**. Hydrogen atoms (except for that on C_{center}) and TfO anion are omitted for clarity. Reagents and conditions (yields): (a) LDA (2 equiv), THF, −78°C 1 h; (b) Ph_2PCl, THF, −78°C, 17 h, then H_2O (35%); (c) $NaNH_2$ or KHMDS, THF or C_6D_6, −78°C to RT, 0.5 h (97%); (d) RT, air, 24 h; **5** (95%), **6** (91%); (e) Amberlite IRA-410 ion-exchange resin (OH^- form), MeOH, RT; **5** (96%), **6** (92%), LDA = lithium diisopropylamide, THF = tetrahydrofuran.

smaller than BPC **A**. The PA(2) of **1** is much smaller than the PA(1). The same observation has been reported by Frenking et al.[1d] PA(1) is mainly determined by the energy level of the highest lying occupied σ orbital of neutral carbones **1**, whereas the PA(2) is mainly determined by the highest lying occupied π orbital of protonated **1·H**.

We attempted to ascertain whether the central carbon of iSPC **1** could actually be employed as a four-electron donor. The desired diaurated complex **2** is efficiently obtained by treating **1** with 2 equivalents of $Ph_3PAuCl/AgBF_4$. This demonstrates the four-electron donor propeties of iSPC **1**. In the ^{31}P NMR spectra, the signal for **2** (28.6, 35.0 ppm) is observed as a singlet. These signals are similar to those of the diaurated complexes of **A**, **E**, and **G**.[6,10] Single crystal X-ray diffraction analysis of **2** confirmed the complexation of the carbon center of **1** to the Au(I) moieties (Scheme 2). The C→Au bond distances of **2** (2.111 and 2.117 Å) are similar to those of diaurated carbone complexes ($\mathbf{A}\cdot(AuCl)_2$: 2.074 and 2.078 Å; $\mathbf{A}\cdot(AuPPh_3)(AuCl)$: 2.080 and 2.127 Å; $Ph_3PCC(OEt)_2\cdot(AuCl)_2$: 2.080 and 2.103 Å; $\mathbf{G}\cdot(AuPPh_3)_2$: 2.118 and 2.127 Å).[4,6,10,13] The Au–Au distance of **2** (2.929 Å) is the slightly longer than that of $\mathbf{G}\cdot(AuPPh_3)_2$ (2.910 Å), while the shorter than those of diaurated carbone complexes ($\mathbf{A}\cdot(AuCl)_2$: 3.143 Å; $\mathbf{A}\cdot(AuPPh_3)(AuCl)$: 3.127 Å; $Ph_3PCC(OEt)_2\cdot(AuCl)_2$: 2.952 Å; $\mathbf{E}\cdot(AuPPh_3)_2$: 3.005 Å).[4,6,10,13] This distance is within the range observed for Au–Au interactions (2.50–3.50 Å).[14] The P→C (**2**: 1.789 Å) and S→C (**2**: 1.728 Å) bond distances are longer than those in **1·H** (P→C: 1.721 Å, S→C: 1.660 Å). The Au←C→Au bond angle (87.7°) in diaurated complex **2** is wider than that of $\mathbf{G}\cdot(AuPPh_3)_2$ (86.5°), while narrower than those of diaurated carbone complexes ($\mathbf{A}\cdot(AuCl)_2$: 98.4°; $\mathbf{A}\cdot(AuPPh_3)(AuCl)$: 96.1°: $Ph_3PCC(OEt)_2\cdot(AuCl)_2$: 89.7°).[4,6,10,13] The P→C←S angles of **2** (112.0°) is narrower than those in **1·H** (122.0°) and $\mathbf{G}\cdot(AuPPh_3)_2$ (115.6°).[6]



Scheme 2. Synthesis and molecular structure of **2**. Hydrogen atoms, BF_4 anions, and solvent molecules (acetone) are omitted for clarity. Reagents and conditions (yields): Ph_3PAuCl (2 equiv) $AgBF_4$ (2 equiv), THF, −78°C, 20 h; (95%).

Conclusions

In conclusion, we have successfully synthesized iSPC derivative **1** bearing a methyl(diphenyl)phosphane ligand. The reactivities of lone pairs at central carbon of **1** predicted by the DFT calculations are demonstrated by the diaurated complex **2**. This study provides a new approach to the synthesis of various iSPC derivatives bearing various phosphane ligand.

Experimental

The reactions were carried out under an atmosphere of dry argon. Reagents were purchased reagent grade from commercial suppliers and used without further purification. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies were recorded on a Bruker Avance 500 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts (δ) in $CDCl_3$ are given in ppm relative to $Si(CH_3)_4$, coupling constants (J) in Hz. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts (δ) in C_6D_6 are calibrated to the residual proton resonance of the solvent (C_6D_6: $\delta H = 7.16$, $\delta C = 128.06$). Chemical shifts for $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy were referenced to an external standard ($C_6H_5CF_3$; $\delta_F = -63.7$, 85% H_3PO_4; 0.0). Iminosulfonium salt **3** was prepared according to the literature.[7]

Compound 1·H

To a suspension of iminosulfonium salt **3** (379 mg, 1.0 mmol) in THF (20 mL) at −78°C was added LDA (1.5 mL, 2.0 M solution in THF/heptane/ethylbenzene, 3.0 mmol). After stirring for 1 h at RT, the solution was cooled to −78°C and a cold THF solution (10 mL, −78°C) of Ph_2PCl (0.2 mL, 0.5 mmol) was added. The resulting solution was stirred overnight. Then, MeTfO (0.11 mL, 1.0 mmol) was added and the reaction mixture was slowly warmed to room temperature over 2 h. The reaction was quenched via the addition of H_2O (10 mL). The water phase was extracted with Et_2O (20 mL × 3). The organic phase was dried ($MgSO_4$) and filtered with DCM. Solvent removal and recrystallization from $MeOH/Et_2O$ afforded **1·H** (88 mg, 30%) as colorless crystal. The solid product of **1·H** suitable for X-ray analysis was recrystallized in $MeCN/Et_2O$ to yield colorless crystals.

1·H: m.p. 161–162°C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (d, $^2J_{PH} = 13.5$ Hz, 3H), 2.62 (s, 3H), 3.68 (d, $^2J_{PH} = 5.5$ Hz, 1H), 7.47–7.52 (m, 10H), 7.59 (td, $J_{HH} = 6.2$ Hz, 1.8 Hz, 2H), 7.67 (dd, $J_{PH} = 13.5$ Hz, 7.5 Hz, 4H), 7.99 (dd, $J_{HH} = 7.5$ Hz, 1.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8 (d, $J_{CP} = 62.4$ Hz, PCH), 18.2 (d, $J_{CP} = 108.7$ Hz, PCH_3), 30.1 (s, NCH_3), 124.5 (d, $J_{CP} = 92.0$ Hz, PC_{ipso}), 127.2, 129.5 (d, $^2J_{CP} = 12.7$ Hz), 129.9, 131.9 (d, $^3J_{CP} = 10.9$ Hz), 133.3, 133.5 (d, $^4J_{CP} = 2.90$ Hz), 139.2 (SC_{ipso}); ^{19}F NMR (470 MHz, $CDCl_3$) δ –79.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ 12.46.

Compound **1·H** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19), C 28 H 27 F 3 N O 3 P S 2, M = 577.6 g mol^{-1}, crystal dimensions 0.27 × 0.17 × 0.10 mm, $a = 10.896(2)$ Å, $b = 13.246(3)$ Å, $c = 19.195(6)$ Å, V = 2770.6(12) Å^3, Z = 4, $\theta_{min} = 3.19°$, $\theta_{max} = 27.46°$, $\rho = 1.385$ g·cm^{-1}, μ (MoK$_\alpha$) = 0.301 mm^{-1}, $F_{000} = 1200$, $-14 \le h \le 13$, $-17 \le k \le 17$, $-24 \le l \le 24$, 27323 reflections measured, 6316 unique ($R_{int} = 0.0873$), $R1 = 0.0563$ ($I > 2.0\sigma$ (I)), Rw = 0.1522 (all data), GooF = 1,043, 349 parameters, 0 restraints.

Compound 1

To a mixture of **1·H** (115 mg, 0.2 mmol) and $NaNH_2$ (15.6 mg, 0.4 mmol) was added THF (10 mL) at RT. The solution was stirred for 0.5 h. After removal of all the volatiles under vacuum, carbone **1** was extracted with Et_2O (10 mL × 3). Concentration of the organic phase in vacuum afforded the desired product as a yellow powder (95 mg, 97%).

1: ^{1}H NMR (500 MHz, C_6D_6) δ 1.78 (d, $^2J_{PH} = 12.5$ Hz, 3H), 3.01 (s, 3H), 6.89–6.92 (m, 2H), 6.99–7.03 (m, 10H), 7.72–7.78 (m, 4H), 8.48–8.50 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 17.3 (d, $^1J_{CP} = 50.3$ Hz, PCH_3), 21.7 (d, $^1J_{CP} = 36.5$ Hz, PCS), 31.0 (s, NCH_3), 128.2, 128.3, 128.4 (d, $J_{CP} = 1.3$ Hz), 129.5, 130.2 (d, $J_{CP} = 2.5$ Hz), 131.6 (d, $J_{CP} = 10.1$ Hz), 136.2 (d, $J_{CP} = 94.3$ Hz, PC_{ipso}), 149.1 (d, $J_{CP} = 13.8$ Hz, SC_{ipso}); ^{31}P NMR (202 MHz, C_6D_6) δ −8.29.

Compound 2

To a mixture of **1** (12.8 mg, 30 μmol) and Ph_3PAuCl (29.7 mg, 60 μmol) was added THF (2 mL) at −78°C. After stirring for 1 h, $AgBF_4$ (11.7 mg, 60 μmol) was added. The resulting solution was stirred overnight. The reaction mixture was filtered through Celite with DCM. Concentration of the filtrate under reduced pressure afforded the desired product (46.5 mg, 95%). The solid product of **2** suitable for X-ray analysis was recrystallized in acetone/Et_2O to yield colorless crystals.

2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.61 (s, 3H), 2.89 (d, $^2J_{PH} = 14.0$ Hz, 3H), 6.94–6.98 (m, 12H), 7.26–7.31 (m, 12H), 7.35–7.38 (m, 4H), 7.46–7.55 (m, 12H), 7.60–7.63 (m, 2H), 8.00–8.01 (m, 4H), 8.04–8.08 (m, 4H); ^{1}H NMR (500 MHz, CD_3CN) δ 2.67 (s, 3H), 2.82 (d, $^2J_{PH} = 12.5$ Hz, 3H), 7.03–7.08 (m, 12H), 7.38–7.43 (m, 16H), 7.48–7.51 (m, 4H), 7.58–7.61 (m, 6H), 7.65–7.70 (m, 4H), 8.02–8.09 (m, 8H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.60, 34.98; ^{31}P NMR (202 MHz, CD_3CN) δ 28.73, 35.40.

Compound **2** crystallizes in the triclinic space group *P–1* (No. 2), C 69 H 68 Au 2 B 2 F 8 N O 2 P 3 S, M = 1635.77 g mol^{-1}, crystal dimensions 0.45 × 0.21 × 0.10 mm, $a = 11.358(9)$ Å, $b = 11.767(1)$ Å, $c = 13.732(6)$ Å, $V = 1637.0(1)$ Å^3, $Z = 1$, $\theta_{min} = 3.06°$, $\theta_{max} = 27.51°$, $\rho = 1.659$ g·cm^{-1}, μ (MoK_α) = 4.649 mm^{-1}, $F_{000} = 806$, $-13 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$, 16022 reflections measured, 12127 unique ($R_{int} = 0.0303$), $R1 = 0.0272$ ($I > 2.0\sigma$ (I)), Rw = 0.728 (all data), GooF = 1,037, 787 parameters, 93 restraints.

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