$C\equiv P$ Ligands

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Making the True "CP" Ligand**

*Joseph G. Cordaro, Daniel Stein, Heinz Rüegger, and Hansjörg Grützmacher**

The quest for cyaphide, the phosphorus equivalent of cyanide, has been a continuous struggle for many years. Potential applications arising from the use of $C\equiv P$ as a bridging ligand between two metals, the incorporation of $C\equiv P$ into coordination polymers and new materials, and the basic synthetic challenges of making $C\equiv P$ have provided inspiration for decades. While phosphaalkynes ($R{-}C\equiv P$) have been known for some time,[1–3] the terminal $M{-}C\equiv P$ has only been reported as a transient species.[4,5] Other C-functionalized $X{-}C\equiv P$ compounds ($X = R_3Si$,[6] R_2N,[7,8] RO,[8] F,[9] Cl,[10]), anionic species $[X{-}C\equiv P]^-$ ($X = R_3B$,[11] RN,[8] O,[12] S[13]), and the cationic phosphonio phosphaalkyne $[R_3P{-}C\equiv P]^+$,[14] have been synthesized, but the vast majority of reports deal with *tert*-butyl,[15] adamantyl,[16] 2,4,6-trimethylphenyl[17] and 2,4,6-tri-*tert*-butylphenyl[18] phosphaalkynes. Recently, we devised a very simple method for accessing the kinetically stable crystalline triphenylmethyl (trityl)-substituted phosphaalkyne, $Ph_3CC\equiv P$ (**1**), which allowed for the economical metal-promoted synthesis of phosphorus heterocycles. However, our ultimate goal and incentive for synthesizing the trityl-substituted phosphaalkyne was to find an adequate leaving group that would lead us to cyaphide.[19]

Treatment of **1** or its complexes $[MH(dppe)_2(Ph_3C{-}C\equiv P)]OTf$ (M = Fe or Ru; dppe = bis(1,2-diphenylphosphinoethane); OTf = trifluoromethanesulfonate) with nucleophiles (Nu) did not furnish the desired cyaphide, $C\equiv P^-$, or its complexes [Eq. (1); electrophile (E) = C].

$$Ph_3E{-}C\equiv P + Nu^- \rightarrow Ph_3E{-}Nu + C\equiv P^- \qquad (1)$$

Therefore, we reasoned that silicon would be more susceptible to nucleophilic attack (E = Si) and applied an analogous synthetic procedure to access the higher homologue $Ph_3SiC\equiv P$ (**3**).

Conversion of Ph_3SiCH_2Cl into the Grignard reagent followed by treatment with PCl_3 produced the silyl-substituted alkyl phosphonous dichloride, $Ph_3SiCH_2PCl_2$ (**2**), in over 87 % yield (Scheme 1). Employing 2.2 equiv of DABCO (1,8-diazabicyclo[2.2.2]octane) effected the dehydrohalogenation reaction, and **2** was fully transformed into the triphenylsilyl-substituted phosphaalkyne **3**. The reaction occurred at ambient temperature and in multiple solvents in less than one hour. (In contrast, the reaction of DABCO with $Ph_3CCH_2PCl_2$ to furnish $Ph_3CC\equiv P$ required a 10-fold excess of base, elevated temperatures, and proceeded best in acetonitrile.[19])

While DABCO alone was effective for the conversion of **2** into **3**, we saw rapid decomposition of this new phosphaalkyne, which was dependent on the solvent. Qualitatively, the rate of decomposition of **3** followed the order $Et_2O \approx$ toluene $<$ THF $\ll CH_3CN$. Suspecting that DABCO-HCl was acting as a soluble source of chloride anion in the more polar solvents that then attacked silicon to produce Ph_3SiCl and the CP anion, which is seemingly unstable under the reaction conditions, we added AgOTf to the reaction mixture. When a solution of **2** in toluene was pretreated with 2.2 equiv of AgOTf for 5 min followed by addition of 2.2 equiv of DABCO, complete conversion into **3** was observed in less than one hour. Filtration through diatomaceous earth to remove insoluble salts furnished indeed a clean solution of **3**, which only slowly decomposed. In the ^{31}P NMR spectrum of **3**, a deshielded signal at $\delta = 111$ ppm was observed. The α-

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[*] Dr. J. G. Cordaro, Dr. D. Stein, Dr. H. Rüegger,
Prof. Dr. H. Grützmacher
Laboratorium für Anorganische Chemie
Departement Chemie und Angewandte Biowissenschaften
ETH Zürich
8093 Zürich (Switzerland)
Fax: (+41) 44-633-1418
E-mail: gruetzmacher@inorg.chem.ethz.ch

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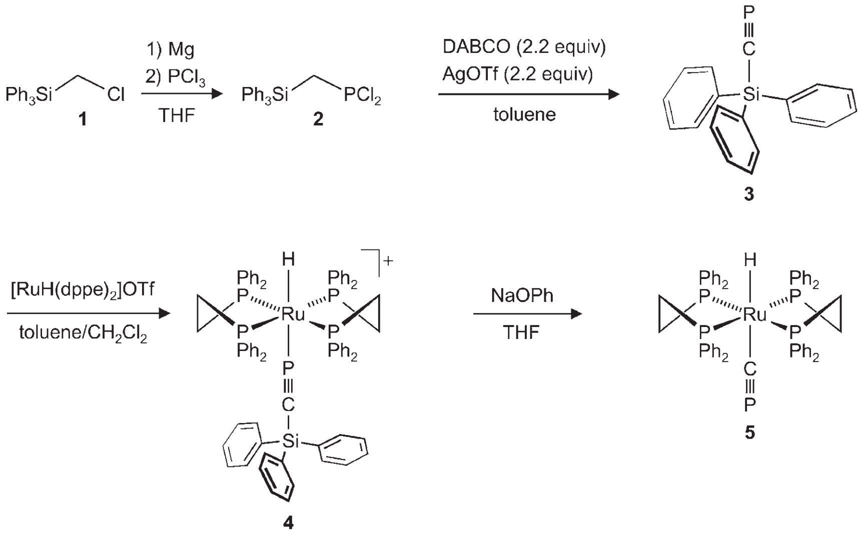

Scheme 1. Synthesis of ruthenium cyaphide complex **5** from the silyl-substituted phosphaalkyne **3** (see text for details).

carbon atom, which gives a signal at $\delta = 193.3$ ppm (d, $J_{\text{C-P}} = 16.4$ Hz) in the ^{13}C NMR spectrum, was also shifted significantly downfield compared to other phosphaalkynes.[20]

Attempts to isolate **3** were unfortunately unsuccessful. If a solution of **3** was concentrated, a red precipitate formed which gave no detectable ^{31}P NMR signal upon redissolving in more polar solvents. However, the lifetime of **3** in toluene or diethyl ether ($t_{1/2} \approx 1$ day at 23 °C) was sufficiently long so that ^{31}P and ^{13}C NMR data could be acquired and, more importantly, coordination of **3** to [RuH(dppe)$_2$]OTf was successful. Addition of a solution of **3** in toluene to 0.5 equiv of [RuH(dppe)$_2$]OTf in CH_2Cl_2 resulted in a color change from dark red to yellow-orange. After workup, the colorless η^1-coordinated complex [RuH(dppe)$_2$($Ph_3SiC{\equiv}P$)]OTf (**4**) was isolated in over 80 % yield as the only product. In the ^{31}P{^{1}H} NMR spectrum, coordination of **3** to the ruthenium cation was confirmed by the downfield-shifted signal at $\delta = 143.8$ ppm for the phosphaalkyne, which appeared as a quintet ($^2J_{\text{P-P}} = 27.8$ Hz) as a result of coupling with the four equivalent phosphorus atoms of the dppe ligands. The dppe ligands were seen as a doublet at $\delta = 60.1$ ppm. A doublet of quintets in the ^{1}H NMR spectrum at $\delta = -8.13$ ppm (*trans*-$^2J_{\text{H-P}} = 122.1$ Hz, *cis*-$^2J_{\text{H-P}} = 17.0$ Hz) for the ruthenium hydride was most diagnostic for the formation of **4**. The signal for the α-carbon atom of the coordinated phosphaalkyne was observed at $\delta = 175.1$ ppm in the ^{13}C NMR spectrum with a significantly larger C–P coupling constant of $J_{\text{C-P}} = 71.4$ Hz as compared to **3**.

The molecular structure of **4** is presented in Figure 1.[21] The X-ray data for **4** are the only available data for any silyl-substituted phosphaalkyne. The P–C bond length (1.530 Å) for **4** is not significantly different when compared to those in the free phosphaalkyne $Ph_3CC{\equiv}P$ (**1**; 1.538 Å) and its iron complex [Fe(dppe)$_2$H($Ph_3CC{\equiv}P$)]OTf (1.535 Å). The deviation from linearity seen in the P-C-Si angle (165.5°) is likewise not unusual and certainly has steric origins.[22]

When **4** was treated with fluoride, no clean reaction occurred. The observation of signals with large P–F couplings in the ^{31}P NMR spectrum of the reaction mixture indicated that phosphorus was attacked by fluoride. Reactions with alkoxides and hydroxide similarly resulted in nucleophilic attack at phosphorus, as indicated by the ^{31}P NMR chemical shifts. However, when **4** was treated with a slight excess of sodium phenoxide (NaOPh) in THF, the immediate formation of an intermediate was observed[23] which was then converted into a new product **5** after 14 h. Product **5** showed a broad signal in the ^{31}P NMR spectrum at $\delta = 165$ ppm, which was weakly coupled to another broad signal at $\delta = 65.2$ ppm. In the ^{1}H NMR spectrum, the hydride appeared as a sextet at $\delta = -11.22$ ppm with $J_{\text{P-H}} \approx 20$ Hz. A ^{31}P-^{1}H HMQC (heteronuclear multiple-quantum correlation) experiment revealed cross-peaks between the hydride and both phosphorus signals. In a selective ^{1}H{^{31}P} NMR experiment, the ^{31}P NMR signal at $\delta = 165$ ppm coupled with the hydride to form a doublet with $J_{\text{P-H}} = 19.5$ Hz, while the signal at $\delta = 65.2$ ppm coupled with the hydride to give a quintet with $J_{\text{P-H}} = 20.5$ Hz. Finally, a ^{13}C-^{1}H HMQC experiment with phosphorus decoupling centered at $\delta = 65$ ppm, detected a cross-peak for a quaternary carbon atom at $\delta = 287.1$ ppm in the ^{13}C dimension, which correlated with the hydride. Coupling between the phosphorus and carbon centers corresponded to $^1J_{\text{C-P}} \approx 90$ Hz. These spectroscopic data are fully consistent

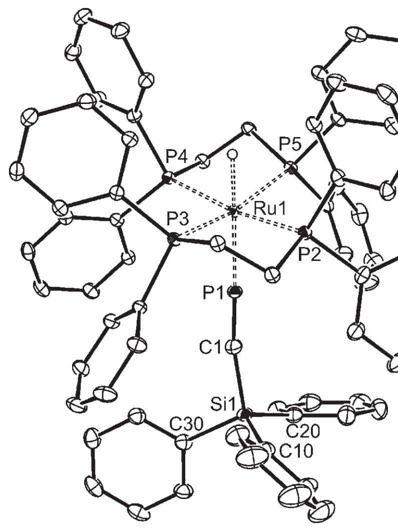

Figure 1. Molecular structure of **4**. The anion and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [°]: P1–C1 1.530(3), C1–Si1 1.825(3), Ru1–P1 2.2485(8), Ru1–P2 2.3811(7), Ru1–P3 2.3721(7), Ru1–P4 2.3559(7), Ru1–P5 2.3694(7); P1-C1-Si1 165.5(2), C10-Si1-C20 114.4(2), C20-Si1-C30 109.0(2), C10-Si1-C30 110.2(2), P1-Ru1-P2 94.79(3), P1-Ru1-P3 94.12(3), P1-Ru1-P4 94.06(3), P1-Ru1-P5 98.34(3), P2-Ru1-P3 82.96(3), P3-Ru1-P4 97.50(3), P4-Ru1-P5 82.63(3), P5-Ru1-P2 95.00(3).

with a {RuH(dppe)$_2$} fragment carrying a CP ligand *trans* to the hydride.

Crystals suitable for X-ray analysis were grown from a THF solution layered with hexane. The results confirm the NMR data and demonstrate the first structurally characterized metal cyaphide complex [RuH(CP)(dppe)$_2$] (**5**; Figure 2). As expected, the CP ligand has rotated from being P-coordinated in the starting complex **4** to C-coordinated in the product **5**. With a CP bond length of 1.573(2) Å, **5** displays the longest reported uncoordinated C–P triple bond, possibly arising from the ability of ruthenium to backbond to the π* orbitals of the CP fragment.

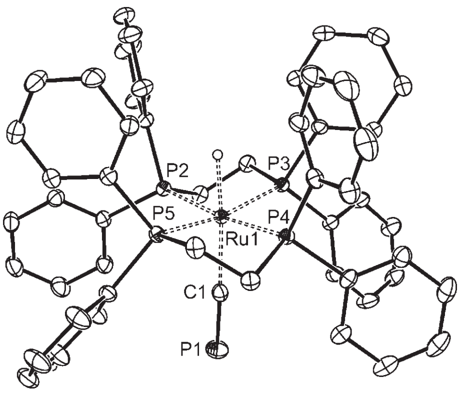

Figure 2. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [°]: P1–C1 1.573(2), Ru1–C1 2.057(2), Ru1–P2 2.3342(5), Ru1–P3 2.3315(5), Ru1–P4 2.3222(5), Ru1–P5 2.3396(4); Ru1-C1-P1 177.9(1), C1-Ru1-P2 92.48(5), C1-Ru1-P3 96.86(5), C1-Ru1-P4 93.74(5), C1-Ru1-P5 94.30(5), P2-Ru1-P3 82.63(2), P3-Ru1-P4 94.60(2), P4-Ru1-P5 83.31(2), P5-Ru1-P2 98.25(2).

An intense band at 1229 cm^{-1} seen in both the Raman and IR spectra was assigned to the CP stretching frequency by comparison with the calculated value of 1336 cm^{-1} (DFT B3LYP/6-31G* for P,C,H; LANL2DZ for Ru). The CP stretching frequency for alkyl-substituted phosphaalkynes is typically found at higher energy (>1500 cm^{-1}), while Willner reported a value of 1468 cm^{-1} for [(CF$_3$)$_3$B(CP)]$^-$.[11] In the solid state, **5** was only moderately air-sensitive. Crystals of **5** were extremely kinetically insoluble in [D$_8$]THF. Although **5** was more soluble in CD$_2$Cl$_2$, a slow reaction was observed that yielded a product identified as [RuHCl(dppe)$_2$] by NMR spectroscopy.

In conclusion, we have reported a rational synthesis to access the first "true" M-CP complex. Using the triphenylsilyl-substituted phosphaalkyne **3**, which functioned with Ph$_3$Si as a protecting group for the CP anion, we were able to effectively deliver cyaphide to ruthenium upon deprotection of the silyl group with phenoxide. We hope that our method for synthesizing Ph$_3$Si–C≡P will be generally applicable and potentially lead to novel M-CP-M complexes.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. NaOPh was synthesized from PhOH and Na in THF. The isolated salt was dried under vacuum at 200 °C. Selected analytical data are given below (see Supporting Information for more details).

Ph$_3$SiCH$_2$PCl$_2$ (**2**): A 250-mL Schlenk flask equipped with a stir bar was charged with freshly ground Mg turnings (10 g, 0.411 mol) and THF (50 mL). Meanwhile, Ph$_3$SiCH$_2$Cl[24] (13.0 g, 0.042 mol) was dissolved in THF (50 mL) in a separate Schlenk flask. The alkyl chloride was slowly added to the Mg turnings in 10 mL portions over 1 h, at which time the Grignard reaction was initiated. An additional 50 mL of THF was used to rinse the remaining alkyl chloride into the reaction mixture. The Grignard reagent was mixed for 3 h and then transferred via cannula to a solution of PCl$_3$ (11 mL, 0.126 mol) in THF (100 mL) cooled to −78 °C. The mixture was stirred and allowed to warm to room temperature over 18 h. After removal of the volatile materials, the gray solid was extracted with toluene (ca. 200 mL) and filtered through diatomaceous earth on a medium-pore fitted glass filter frit. The volatile materials were removed under reduced pressure to furnish a white solid. Crystallization from THF/hexane at −30 °C afforded analytically pure material (13.8 g, 87.6 %); m.p.: 96–97 °C; ^{1}H NMR (300 MHz, C$_6$D$_6$, 23 °C): $\delta=2.60$ ppm (d, $^2J_{\text{H-P}}=14.3$ Hz, 2 H); ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$, 23 °C): $\delta=32.52$ ppm (d, $J_{\text{C-P}}=64.6$ Hz); ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 23 °C): $\delta=199.7$ ppm.

Ph$_3$SiC≡P (**3**): A 20-mL scintillation vial equipped with a stir bar was charged with Ph$_3$SiCH$_2$PCl$_2$ (**2**; 0.375 g, 1.00 mmol), AgOTf (0.564 g, 2.20 mmol), and toluene (18 mL). The suspension was protected from light and vigorously stirred. After 5 min, DABCO (0.248 g, 2.20 mmol) was added to the vial and stirring was continued. After an additional 60 min, the mixture was filtered through a pad of diatomaceous earth on a medium-pore fitted glass filter frit eluting with toluene (ca. 10 mL). The resulting yellow solution was used immediately. ^{13}C{^{1}H} NMR (75.5 MHz, Et$_2$O, 23 °C): $\delta=193.3$ ppm (d, $^1J_{\text{C-P}}=16.4$ Hz); ^{31}P{^{1}H} NMR (121.5 MHz, Et$_2$O, 23 °C): $\delta=111.3$ ppm.

[RuH(dppe)$_2$(Ph$_3$SiC≡P)]OTf (**4**): A 250-mL Schlenk flask equipped with a stir bar was charged with [RuH(dppe)$_2$]OTf[25] (0.524 g, 0.500 mmol) and CH$_2$Cl$_2$ (80 mL). The silyl-substituted phosphaalkyne **3** (1.0 mmol, 2 equiv) synthesized above was added via cannula transfer, resulting in a color change from red to light orange. After 1 h, the solution was concentrated to approximately 40 mL under reduced pressure which resulted in copious amounts of white precipitate. The suspension was mixed for 2 h then allowed to settle. The mother liquor was removed via cannula filtration, and the faint yellow solid was washed with diethyl ether (3 × 10 mL). Excess solvent was removed under reduced pressure to furnish a white solid (0.576 g, 84.5 %). Analytically pure material was obtained through crystallization from THF/toluene; m.p.: 185 °C (dec.); ^{1}H NMR (300 MHz, [D$_8$]THF, 23 °C): $\delta=-8.13$ ppm (dqnt, *trans*-$^2J_{\text{P-H}}=122.1$ Hz, *cis*-$^2J_{\text{P-H}}=17.0$ Hz, 1 H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF, 23 °C): $\delta=175.1$ ppm (d, $^1J_{\text{C-P}}=71.4$ Hz); ^{19}F NMR (188 MHz, [D$_8$]THF, 23 °C): $\delta=-78.4$ ppm; ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF, 23 °C): $\delta=143.8$ ppm (qnt, $^2J_{\text{P-P}}=27.8$ Hz, 1 P), 60.1 ppm (d, $^2J_{\text{P-P}}=27.3$ Hz, 4 P).

[RuH(dppe)$_2$(C≡P)] (**5**): A 20-mL vial equipped with a stir bar was charged with **4** (0.270 g, 0.20 mmol) and THF (18 mL). The solid dissolved after stirring for 5 min. The solution was then cooled to −30 °C, and NaOPh (0.032 g, 0.276 mmol) in THF (2 mL) was added. The solution was warmed to 23 °C over 30 min. After mixing for 14 h, the yellow-orange solution was filtered through a pad of silica gel, eluting with THF (5 mL). After removal of the volatile materials, the solid was washed with CH$_3$CN (2 × 10 mL) then redissolved in THF (ca. 15 mL) and filtered through diatomaceous earth in a Pasteur filter pipette. Excess solvent was removed under reduced pressure to furnish a yellow solid (0.135 g, 71.8 %). This product was > 95 % pure by NMR spectroscopy. Crystallization from THF/hexane furnished analytically pure material, which was also suitable for X-ray analysis (0.60 g, 31.9 %); m.p. > 198 °C (decomp); ^{1}H NMR (300 MHz, [D$_8$]THF, 23 °C): $\delta = -11.22$ ppm (dqnt, *cis*-$^2J_{\text{H-P}} = 20.7$ Hz, *trans*-$^3J_{\text{H-P}} = 20.4$ Hz, 1 H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF, 23 °C): $\delta = 287.1$ ppm (m); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF, 23 °C): $\delta = 165.0$ (br, 1 P), 65.2 ppm (br, 4 P); Raman: $\tilde{\nu} = 1885$ (w, Ru-H), 1228 (vs, C≡P).

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[21] Structural data for **4**: Colorless, air-sensitive single crystals of **4** used for X-ray analysis had the composition [RuH(dppe)$_2$-(Ph$_3$SiC≡P)](BF$_4$)$_{0.94}$(Cl)$_{0.06}$ and were obtained from the reaction starting from [RuH(dppe)$_2$]BF$_4$ rather than the OTf salt and recrystallized from CH$_2$Cl$_2$ layered with hexane at 23 °C; $C_{72}H_{66}B_{0.94}Cl_{0.06}F_{3.76}P_5RuSi$; tetragonal; space group *I*4(1)/*a*; $a = 40.152(2)$, $b = 40.152(2)$, $c = 16.203(1)$ Å; $V = 26121(3)$ Å^3; $Z = 16$; $\rho_{\text{calcd}} = 1.393$ Mg m^{-3}; crystal dimensions $0.46 \times 0.25 \times 0.14$ mm^3; Bruker SMART Apex diffractometer with CCD area detector; Mo$_{K\alpha}$ radiation (0.71073 Å), 150 K, $2\Theta_{\max} = 56.66°$; 95351 reflections, 16245 independent ($R_{\text{int}} = 0.0607$); direct methods; empirical absorption correction SADABS (v2.03); refinement against full matrix (versus F^2) with SHELXTL (v6.12) and SHELXL-97; 787 parameters, 3 restraints (BF$_4$/Cl, Ru-H), $R1 = 0.0487$ and w$R2$(all data) = 0.1321, max/min residual electron density: 1.140/−1.329 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. The dichloromethane molecule in the crystal lattice is slightly disordered. Structural data for **5**: Pale yellow, air-sensitive single crystals were obtained from a THF/hexane solution of **5** at room temperature; $C_{53}H_{49}P_5Ru$; monoclinic; space group *P*2(1)/*n*; $a = 10.8585(6)$, $b = 24.019(1)$, $c = 17.5981(9)$ Å; $V = 4481.3(4)$ Å^3; $Z = 4$; $\rho_{\text{calcd}} = 1.396$ Mg m^{-3}; crystal dimensions $0.30 \times 0.26 \times 0.26$ mm^3; Bruker SMART Apex diffractometer with CCD area detector; Mo$_{K\alpha}$ radiation (0.71073 Å), 200 K, $2\Theta_{\max} = 56.68°$; 33735 reflections, 11153 independent ($R_{\text{int}} = 0.0258$); direct methods; refinement against full matrix (versus F^2) with SHELXTL (v6.12) and SHELXL-97; 536 parameters, 1 restraint (Ru-H), $R1 = 0.0323$ and w$R2$(all data) = 0.0888, max/min residual electron density 0.862/−0.251 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. CCDC 611173 (**4**) and 611174 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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