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Synthesis of Functionalized Vinylgermanes through a New Ruthenium-Catalyzed Coupling Reaction

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Abstract: Vinyl-substituted germanes react stereo- and regioselectively with olefins in the presence of complexes containing Ru−H and Ru−Ge bonds with the formation of functionalized vinylgermanes that cannot be synthesized by olefin cross-metathesis procedures. The reaction opens a new catalytic route for preparation of a class of organogermanes that are potent organometallic reagents for organic synthesis because they show very low toxicity and could replace organotin compounds. The mechanism of this new catalytic route was proven to involve an interesting insertion of the vinylgermane into the Ru−H bond and β-Ge transfer to the metal with elimination of ethylene and generation of an Ru−Ge bond, followed by insertion of the alkene into the Ru−Ge bond and β-H transfer to the metal to eliminate the substituted vinylgermane.

Keywords: alkenes · germanium · homogeneous catalysis · ruthenium · vinylgermanes

Introduction

While the synthetic utility of organosilicon and organotin compounds has been extensively studied, organogermanium compounds have attracted less attention in synthetic organic chemistry, presumably because of the scarce commercial availability of chlorogermanium compounds to act as sources of starting substances. However, organogermanium compounds have recently been recognized as important compounds for organic synthesis.[1,2] Alkenylgermanes in particular show a very low toxicity[3] and, therefore, they could serve as alternatives to the organotin reagents. Functionalized vinylgermanes used in organic synthesis can be prepared by various methodologies involving classical stoichiometric organometallic routes, as well as by hydrogermylation and bisgermylation of alkynes and by dehydrogenative germylation of alkenes (for reviews, see reference [4]). The latter reaction, which is analogous to dehydrogenative silylation, is catalyzed by ruthenium and rhodium complexes and produces substituted vinylgermanes accompanied by hydrogenated products.[5] Transition-metal-catalyzed hydrogermylation of alkynes proceeds in good yield but usually leads to a mixture of stereo- and regioisomers.[6] Only the addition of germanes to alkynols and silylacetylene catalyzed by rhodium(I) complexes gives alkenylgermanes in high yield and with good selectivity.[7] Also, the addition of M−Ge compounds (where M = Si, B, Sn, B, or Se) to arylacetylenes catalyzed by palladium complexes gives, very often selectively, ethene products substituted with germanium and other heteroatoms and metals (see reference [4] and references therein). Recently, much attention has been focused on the functionalized vinylgermanes because pyridyl(germyl)ethene, for example, was reported to undergo cycloaddition with nitrile oxide to form (germyl)isoxazolines possessing vasodilating, antithrombotic, and cardio-protective activities.[8] To produce such isoxalolines, the use of stereodefined germylethene derivatives is essential.

In last two decades we have developed two universal methods for the synthesis of well-defined molecular compounds with vinylsilicon functionalities. Both methods, that is, silylative coupling (also called *trans*-silylation or silylgroup transfer) and cross-metathesis, are based on catalytic transformations of vinylsilicon compounds with olefins and lead to the synthesis of functionalized vinylsilicon reagents. For a recent review of these methods, see reference [9].

While cross-metathesis (CM) is catalyzed by well-defined Ru and Mo–carbene complexes, silylative coupling (SC) takes place in the presence of complexes initiating or gener-

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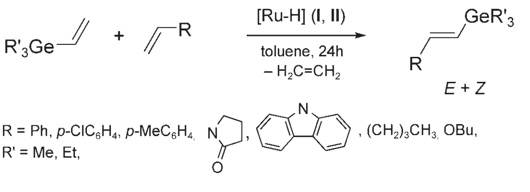
ating M–H and M–Si bonds (where M = Ru, Rh, or Ir). The latter reaction proceeds through cleavage of the =C–Si bond of the vinyl-substituted silicon compound and activation of the =C–H bond of the olefin (or the vinylsilane molecule in the homocoupling). The mechanism of SC, determined by Wakatsuki et al.[10] and by our group,[11] involves an insertion of the vinylsilane into the M–H bond and β Si transfer to the metal with elimination of ethylene to generate the M–Si species, followed by insertion of the alkene into the M–Si bond and β-H transfer to the metal, with elimination of the substituted vinylsilane. We have recently found that this mode of reactivity, which is well known for vinylsilanes, seems to be general and is also exhibited by vinylboronates[12] and vinylgermanes. Herein, we report a new catalytic transformation of vinyl-trisubstituted germanes with selected alkenes, in the presence of ruthenium complexes with a Ru–H bond.

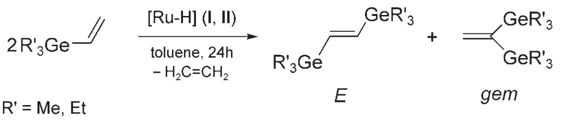
Results and Discussion

The complexes [RuH(Cl)(CO)(PCy$_3$)$_2$] (**I**; Cy = cyclohexyl) and [RuH(Cl)(CO)(PPh$_3$)$_3$] (**II**) catalyze the reaction of vinylgermanes with selected alkenes according to the non-metallacarbene mechanism, thereby leading to effective formation of vinylgermanium derivatives [Eq. (1)].



(1)

A three- to tenfold excess of olefin over vinylgermane was used to avoid homocoupling of the vinylgermane. The homocoupling process occurs readily in the presence of **I** to yield finally a mixture of two products [Eq. (2)], but with high preference for the *E* product.



(2)

Heterocoupling (*trans*-germylation) of alkenes with vinylgermanes proceeds very efficiently, also yielding predominantly *E* products, according to Equation (1). *trans*-Germylation of styrenes, vinylcarbazole, or vinylpirrolidone with vinyltrialkylgermanes proceeds stereo- and regioselectively to give exclusively *E* isomers (more than 97%); only for vinyl ether was a mixture of *E* and *Z* products noticed, with a preference for the *E* isomer. Since olefin isomerization also occurs in the presence of ruthenium hydride complexes, a mixture of alkenylgermanes (with a high predominance of (*E*)-1,2-alkenylgermane) is formed in the germylative coupling of 1-hexene but is accompanied by hexene isomers. *trans*-Germylation took a longer time than silylation coupling and also, in a few cases, required the presence of 2% catalyst, rather than 1% as in the *trans*-silylation.[11b]

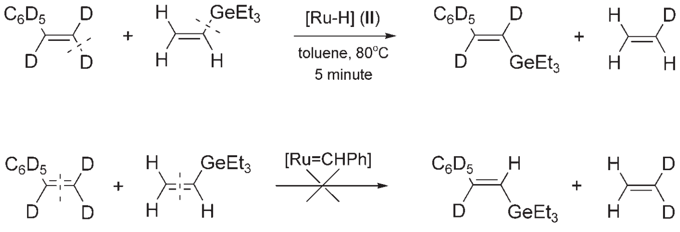
When 1-alkenes were used as cosubstrates the formation of some amounts of vinylgermane homocoupling products could not be avoided, even with a fivefold excess of the alkene. The results obtained are compiled in Table 1. In the presence of ruthenium–carbene complexes, that is, Grubbs catalyst [Cl$_2$Ru(=CHPh)(PCy$_3$)$_2$] (**IV**; the first generation) and [(H$_2$IMes)RuCl$_2$(=CHPh)(PCy$_3$)] (**V**; the second generation; Mes = 2,4,6-trimethylphenyl) no self- or cross-metathesis reactions occurred.

Table 1. Catalytic transformation of vinylgermanes through homo- and cross-coupling reactions catalyzed by complex **I**.[a]

VinylGeR$_3$	R group in H$_2$C=CH–R	*T* [°C]	Yield [%] (selectivity *E*/*Z*/*gem* [%])
vinylGeMe$_3$	Ph	110[a]	90 (95/1/4)
vinylGeMe$_3$	GeMe$_3$	110[a,b]	85 (90/0/10)
vinylGeEt$_3$	Ph	80	98 (100/0/0)
vinylGeEt$_3$	Ph	80[c]	98 (100/0/0)
vinylGeEt$_3$	*p*ClC$_6$H$_4$	80	> 99 (100/0/0)
vinylGeEt$_3$	*p*MeC$_6$H$_4$	80	> 99 (100/0/0)
vinylGeEt$_3$	C$_4$H$_9$	100[a]	62[d]
vinylGeEt$_3$	OC$_4$H$_9$	65[e,f]	96 (65/35/0)
vinylGeEt$_3$	9-carbazole	110[f]	97 (100/0/0)
vinylGeEt$_3$	2-pyrrolidinone	100	99 (100/0/0)
vinylGeEt$_3$	GeEt$_3$	120[a,b]	83 (100/0/0)

[a] Reaction conditions unless stated otherwise: open system, toluene (0.5 M), $t = 24$ h, [RuH(Cl)(CO)(PCy$_3$)$_2$]:[CH$_2$=CHGe]:[olefin] = 1×10^{-2}:1:3. The product yields were determined by GC, and the selectivity was confirmed by GC-MS and ^{1}H NMR spectroscopy. [b] Closed system. [c] Toluene (1 M). [d] **III** (see below) used as the catalyst, $t = 3$ h. [e] 37% *E* accompanied by other isomers. [f] [CH$_2$=CHGe]:[olefin] = 1:10. [g] [Ru]:[CH$_2$=CHGe] = 2×10^{-2}:1.

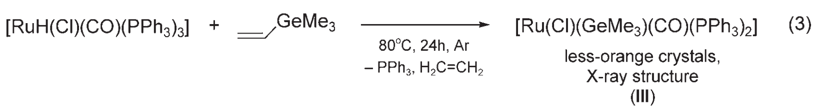
Nonisolated products were identified on the basis of GC-MS spectra. To confirm the non-metallacarbene mechanism of *trans*-germylation (versus the metallacarbene scheme), the reactions of [D$_8$]styrene with vinyltriethylgermane catalyzed by **II** were studied according to procedures previously described.[11c] In this situation the formation of [D$_7$]germylstyrene and [D$_1$]ethylene is to be expected (Scheme 1). By contrast, the metallacarbene mechanism would afford [D$_6$]germylstyrene and [D$_2$]ethylene.



Scheme 1. Formation of *trans*-germylation products through the non-metallacarbene mechanism (top) and the metallacarbene mechanism (bottom).

Analysis of the reaction mixture after 5 min and 30 min, that is, in the initial stages of the reaction when conversion had not exceeded 1 % and 10 %, respectively, revealed only the formation of [D_7]germylstyrene. Therefore, the metallacarbene mechanism can be excluded. However, to provide additional evidence for this new vinylgermane catalytic transformation, a series of stoichiometric reactions of olefins with ruthenium complexes was studied.

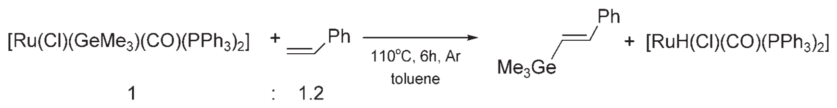
The reaction of equimolar amounts of **I** with vinylgermane was carried out to yield ruthenium–germyl complex **III**; ^{1}H NMR spectroscopy provided evidence (at $\delta = 5.25$ ppm) of ethylene evolution in the reaction mixture occurring according to Equation (3).



The formation of the Ru–Ge bond proceeds through migratory insertion of the vinylgermane into the Ru–H bond followed by β Ge transfer to eliminate ethylene, as proposed in Scheme 2. Such a transformation (and the product in Equation (3)) has not been previously reported in literature to the best of our knowledge. Complex **III** was isolated and characterized by spectroscopic and analytical methods and its X-ray crystal structure was determined (see Figure 1). The ruthenium center is five-coordinate and the coordination polyhedron is a slightly distorted tetragonal pyramid, with phosphine, chlorine, and carbon atoms at the base and a germanium atom at the apex. The two triphenylphosphine groups are *trans* with respect to each other.

A similar geometry was found in related compounds with a trialkyl- or trialkoxysilicon–ruthenium bond: [Ru($SiEt_3$)(Cl)(CO)(PPh_3)$_2$] and [Ru(Si($OEt)_3$))(Cl)(CO)(PPh_3)$_2$] (however, no detailed structural data are available),[13a] as well as [Ru($SiMe_3$)(Cl)(CO)(PPh_3)$_2$].[13b]

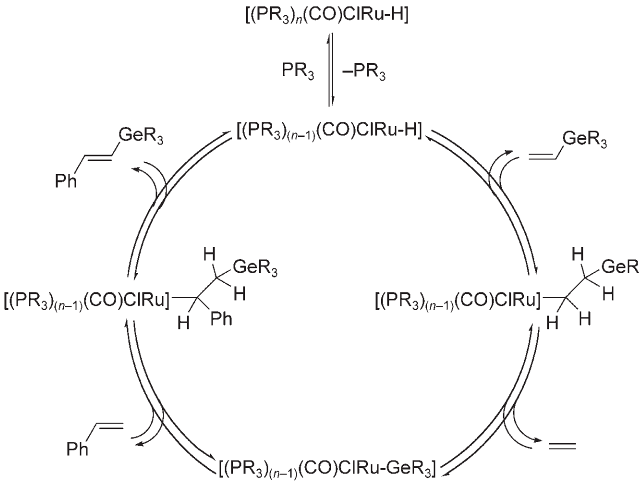
The synthesis of the new Ru–Ge complex was tested in a reaction with a twofold excess of styrene. The reaction yielded (*E*)-styrylgermane (identified by NMR spectroscopy and GC-MS) and the hydride complex [RuH(Cl)(CO)(PPh_3)$_2$] according to the proposed Equation (4).



The mechanistic scheme of this new type of vinylgermane conversion, examined for the reaction with styrene, involves insertion of vinylgermane into the Ru–H bond followed by β-Ge elimination of ethylene (Scheme 2) and the migratory insertion of styrene, as a representative alkene (or vinylgermane in the case of homocoupling), into the Ru–Ge bond followed by β-H elimination to give (*E*)-phenyl(germyl)ethene. Dissociation of phosphine is postulated to generate the catalytic Ru–H species. Additional experiments, performed with a slight excess of phosphine, have evidenced strong retardation of this process. High catalytic activity of Ru–Ge complex **III** strongly supports this mechanism.

Conclusion

Germylation of non-isomerizing olefins with vinyl-trisubstituted germanes in the presence of catalysts containing Ru–H bonds opens a new effective catalytic route for the synthesis of functionalized vinylgermanes which could be very useful as organometallic reagents in organic synthesis. Unlike the analogous vinylsilanes[9] and vinylboronates,[12] such functionalized vinylgermanes cannot be synthesized by the metathesis procedure. A formation of a Ru–Ge intermediate proceeds through a new step-migratory insertion of vinylgermane into the Ru–H bond, followed by β-Ge transfer with elimination of ethylene.



Scheme 2. Mechanistic scheme for *trans*-germylation of styrene with vinylgermanes.

Experimental Section

General methods: ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and DEPT spectra were recorded on Varian XL 300 MHz spectrometer in $CDCl_3$ (or C_6D_6) solution. Chemical shifts (δ) are reported in ppm with reference to the residual solvent (CH_3Cl) peak for ^{1}H and ^{13}C NMR spectra. GC analyses were performed on a Varian 3300 instrument with a DB-5 fused-silica capillary column (30 m × 0.15 mm) and a thermal conductivity de-

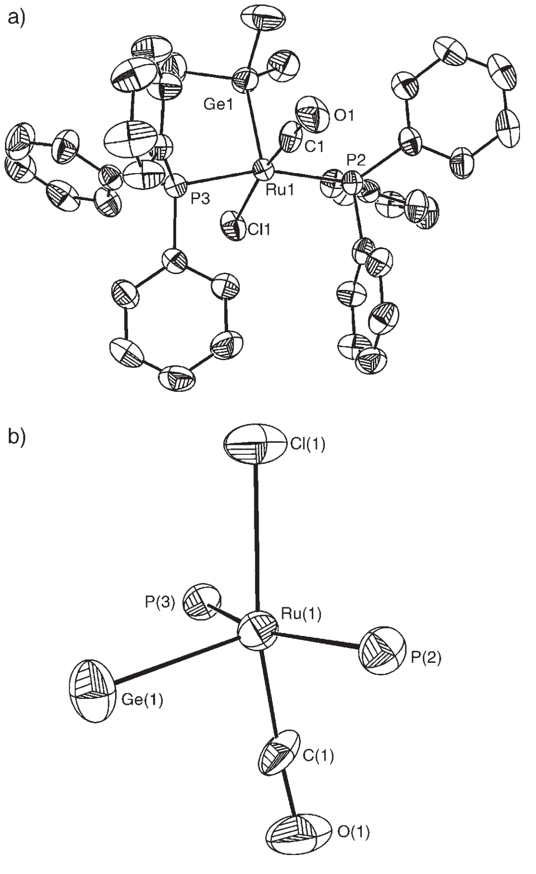


Figure 1. a) Anisotropic displacement ellipsoid representative structure of complex **III**. Hydrogen atoms have been removed for clarity. b) Perspective view of the structure of complex **III**.

tector (TCD). Mass spectra of the monomers and products were obtained by GC-MS analysis on a Varian Saturn 2100T instrument, equipped with a BD-5 capillary column (30 m) and an ion-trap detector. HRMS analyses were performed on an AMD-402 mass spectrometer (AMD Intectra GmbH). Thin-layer chromatography was performed on plates coated with a 250 µm layer of silica gel (Aldrich and Merck); column chromatography was conducted with silica gel 60 (70–230 mesh; Fluka). Melting points are uncorrected and were determined by using an SMP3 melting point apparatus (BIBBY Stuart Scientific, UK). Toluene and pentane were dried by distillation from sodium hydride; similarly hexane was distilled from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under a dry argon atmosphere.

Materials: The chemicals were obtained from the following sources: toluene, dodecane, pentane, and hexane were purchased from Fluka; $CDCl_3$ and C_6D_6 were obtained from Dr. Glaser AG, Basel; 9-vinylcarbazol, 1-vinyl-2-pyrrolidinone, styrene, hexene, vinyl-*n*-butyl ether, and the Grubbs catalysts $[RuCl_2(PCy_3)_2(=CHPh)]$ (**IV**) and $[RuCl_2(PCy_3)(IMesH_2)(=CHPh)]$ (**V**) were bought from Aldrich; triethylbromogermane and trimethylchlorogermane were purchased from Gelest. The ruthenium complexes $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**)[13a] and $[RuH(Cl)(CO)(PPh_3)_3]$ (**II**)[13b] were prepared according to the literature procedures.

Representative procedure for *trans*-germylation: In a typical test, the ruthenium catalyst $[RuH(Cl)(CO)(PCy_3)_2)]$ (**I**; 1 or 2 mol %) was dissolved in toluene and placed in a glass ampoule under argon. The reagents and dodecane as an internal standard (5 % by volume of all components) were then added (usually in a molar ratio: for homogermylation $[Ru]:[CH_2{=}CHGe] = 1\times10^{-1}:1$, for cross-germylation $[Ru]:[CH_2{=}CHGe]:[olefin] = 1\times10^{-1}(or\ 2\times10^{-1}):1:3(10)$). After that, the ampoule was heated at 65–120 °C for 24 h. The final products were separated from the residues of the catalyst and the remains of styrene by using a column of silica. The progress of the both reactions was controlled by GC and GCMS.

Syntheses:

(*E*)-1,2-Bis(triethylgermane)ethene (1): $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) complex (23 mg, 0.032 mmol), toluene (5.75 mL), and triethylvinylgermane (0.592 g, 3.17 mmol) were placed in a 15-mL glass ampoule. The ampoule was closed and heated under argon at 120 °C for 24 h. The final product was separated from the residues of the catalyst and reactants by using a column of silica (eluent: hexane; $R_f = 0.50$) to afford **1** (0.301 g, 0.89 mmol, 56 % isolated yield) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta = 0.78$ (q, 12 H; CH_2), 1.01 (t, 18 H; CH_3), 6.53 ppm (s, 2 H; HC=CH); ^{13}C NMR ($CDCl_3$): $\delta = 4.28$ (CH_2), 9.05 (CH_3), 146.84 ppm (HC=CH); MS (EI): *m*/*z* (%): 317 $[M^{+\cdot}-CH_2CH_3]$ (82), 316 $[M^{+\cdot}-CH_2{=}CH_2]$ (82), 288 $[M^{+\cdot}-2\times CH_2CH_3]$ (15), 162 (100), 133 (70), 101 (40), 73 (16); elemental analysis calcd (%) for $C_{14}H_{32}Ge_2$: C 48.64, H 9.33; found: C 48.70, H 9.41.

Mixture of (*E*)-1,2-bis(trimethylgermane)ethene (2a) and 1,1-bis(trimethylgermane)ethene (2b): $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) complex (30 mg, 0.041 mmol), toluene (3.43 mL), and trimethylvinylgermane (0.598 g, 4.13 mmol) were placed in a 15 mL glass ampoule. The ampoule was closed and heated under argon at 110 °C for 24 h. The final products were separated from the residues of the catalyst and reactants by distillation to afford a mixture of **2a** and **2b** (0.426 g, 1.97 mmol, 79 % isolated yield, *E*:*gem* 90:10) as a colorless liquid: **2a**: ^1H NMR (C_6D_6): $\delta = 0.27$ (s, 18 H; CH_3), 6.85 ppm (s, 2 H; HC=CH); ^{13}C NMR (C_6D_6): $\delta = 1.38$ (CH_3), 149.13 ppm (HC=CH); MS (EI): *m*/*z* (%): 262 $[M^+]$ (1), 247 $[M^+-CH_3]$ (100), 219 (4), 145 (3), 119 (30), 102 (3), 89 (3), 75 (1); **2b**: ^1H NMR (C_6D_6): $\delta = 0.30$ (s, 18 H; CH_3), 6.23 ppm (s, 2 H, $H_2C{=}$); ^{13}C NMR ($CDCl_3$): $\delta = -0.99$ (CH_3), 125.66 (c_i), 135.56 ppm (H_2C); MS (EI): *m*/*z* (%): 262 $[M^{+\cdot}]$ (4), 247 $[M^{+\cdot}-CH_3]$ (87), 221 (20), 193 (5), 130 (6), 119 (100), 104 (14), 89 (23), 73 (7).

(*E*)-1-Phenyl-2-(trimethylgermane)ethene (3): $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) complex (29 mg, 0.040 mmol), toluene (5.94 mL), trimethylvinylgermane (0.578 g, 3.99 mmol), and styrene (1.25 g, 11.97 mmol) were placed in a 15-mL glass ampoule. The ampoule was closed and heated under argon at 110 °C for 24 h. ^1H NMR (C_6D_6): $\delta = 0.19$ (s, 9 H; CH_3), 6.66 (d, 1 H, $J_{H,H} = 18{,}9$ Hz; Ge−HC=C*H*), 6.91 (d, 1 H, $J_{H,H} = 18.6$ Hz; Ge−*H*C=CH), 7.05–7.35 ppm (m, 5 H; C_6H_5); MS (EI): *m*/*z* (%): 222 $[M^{+\cdot}]$ (6), 207 $[M^{+}\cdot-CH_3]$ (100), 191 (6), 177 (6), 151 (5), 117 (15), 103 (20), 89 (10), 77 (8), 50 (7); HRMS: calcd for $C_{11}H_{16}Ge$: 222.04638; found: 222.04658; elemental analysis calcd (%) for $C_{11}H_{16}Ge$: C 59.81, H 7.30; found: C 59.92, H 7.35.

(*E*)-1-Phenyl-2-(triethylgermane)ethene (4): $[RuH(Cl)(CO)(PCy_3)_2]$ (**I**) complex (21 mg, 0.029 mmol), toluene (4.25 mL), triethylvinylgermane (0.540 g, 2.89 mmol), and styrene (0.903 g, 8.67 mmol) were placed in a 15 mL glass ampoule. The ampoule was heated under argon at 80 °C for 24 h. The final product was separated from the residues of the catalyst and reactants by using a column of silica (eluent: hexane; $R_f = 0.75$) to afford **4** (0.707 g, 2.69 mmol, 93 % isolated yield) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta = 0.88$ (q, 6 H; CH_2), 1.07 (t, 9 H; CH_3), 6.62 (d, 1 H, $J_{H,H} = 18.9$ Hz; Ge−HC=C*H*), 6.83 (d, 1 H, $J_{H,H} = 18.9$ Hz; Ge−*H*C=CH), 7.25 (d, 1 H, $J_{H,H} = 7.5$ Hz; *p*-C_6H_5), 7.33 (t, 2 H; *m*-C_6H_5), 7.44 ppm (d, 2 H, $J_{H,H} = 6.9$ Hz; *o*-C_6H_5); ^{13}C NMR ($CDCl_3$): $\delta = 4.39$ (CH_2), 8.94 (CH_3), 126.13 (*o*-C_6H_5), 127.59 (*p*-C_6H_5), 127.80 (Ge−HC=*C*H), 128.47 (*m*-C_6H_5), 138.41 (c_i-C_6H_5), 143.28 ppm (Ge−H*C*=CH); MS (EI): *m*/*z* (%): 264 $[M^{+\cdot}]$ (3), 249 $[M^{+\cdot}-CH_3]$ (1), 235 $[M^{+\cdot}-CH_2CH_3]$ (100), 234 $[M^{+\cdot}-CH_2{=}CH_2]$ (39), 207 (31), 177 (19), 151 (9), 131 (5), 103 (11), 77 (5); HRMS: calcd for $C_{14}H_{22}Ge$: 264.09333; found: 264.09383; elemental analysis calcd (%) for $C_{14}H_{22}Ge$: C 63.94, H 8.43; found: C 63.99, H 8.52.

(*E*)-1-(*p*-Chlorophenyl)-2-(triethylgermane)ethene (5): Compound **5** was prepared from the appropriate starting materials according to the above procedure for **4**. The reaction afforded **5** (0.816 g, 2.75 mmol, 95 % isolated yield) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta = 0.84$ (q, 6 H; CH_2), 1.03 (t, 9 H; CH_3), 6.56 (d, 1 H, $J_{H,H} = 18.9$ Hz; Ge−HC=C*H*), 6.83 (d, 1 H, $J_{H,H} = 18.9$ Hz; Ge−*H*C=CH), 7.25 (d, 2 H, $J_{H,H} = 8.7$ Hz; *m*-C_6H_4Cl), 7.31 ppm (d, 2 H, $J_{H,H} = 8.7$ Hz; *o*-C_6H_4Cl); ^{13}C NMR ($CDCl_3$): $\delta = 4.34$ (CH_2), 8.93 (CH_3), 127.32 (*o*-C_6H_4Cl), 128.59 (*m*-C_6H_4Cl), 128.85 (Ge−

HC=*C*H), 133.15 (c_i), 136.84 (c_i), 141.90 ppm (Ge−H*C*=CH); MS (EI): *m*/*z* (%): 298 [$M^{+\cdot}$] (1), 269 [$M^{+\cdot}-CH_2CH_3$] (100), 241 (49), 211 (22), 183 (8), 131 (8), 103 (19), 75 (13); HRMS: calcd for $C_{14}H_{21}ClGe$: 298.05436; found: 298.05476; elemental analysis calcd (%) for $C_{14}H_{21}ClGe$: C 56.54, H 7.12; found: C 56.63, H 7.22.

(*E*)-1-(*p*-Methylphenyl)-2-(triethylgermane)ethene (6): Compound **6** was prepared from the appropriate starting materials according to the above procedure for **4**. The reaction afforded **6** (0.752 g, 2.72 mmol, 94 % isolated yield) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta=0.87$ (q, 6H; CH_2), 1.07 (t, 9H; CH_3), 2.36 (s, 3H; CH_3) 6.56 (d, 1H, $J_{H,H}=19.2$ Hz; Ge−HC=C*H*), 6.81 (d, 1H, $J_{H,H}=18.9$ Hz; Ge−*H*C=CH), 7.15 (d, 2H, $J_{H,H}=8.1$ Hz; *m*-$C_6\mathit{H}_4CH_3$), 7.34 ppm (d, 2H, $J_{H,H}=8.4$ Hz; *o*-$C_6\mathit{H}_4CH_3$); ^{13}C NMR ($CDCl_3$): $\delta=4.52$ (CH_2), 9.06 (CH_3), 125.93 (*o*-$\mathit{C}_6H_4CH_3$), 126.23 (Ge−HC=*C*H), 129.06 (*m*-$\mathit{C}_6H_4CH_3$), 135.64 (c_i), 137.29 (c_i), 143.00 ppm (Ge−H*C*=CH); MS (EI): *m*/*z* (%): 278 [$M^{+\cdot}$ (1), 250 [$M^{+\cdot}-CH_2{=}CH_2$] (19), 249 [$M^{+\cdot}-CH_2CH_3$] (58), 248 (100), 221 (38), 191 (23), 163 (16), 131 (6), 115 (12), 103 (12), 91 (11), 75 (6); HRMS: calcd for $C_{15}H_{24}Ge$: 278.10898; found: 278.10105; elemental analysis calcd (%) for $C_{15}H_{24}Ge$: C 65.04, H 8.73; found: C 65.11, H 8.84.

Triethylhexenylgermanes (7): [RuH(Cl)(CO)(PCy_3)$_2$] (**I**) complex (25 mg, 0.034 mmol), toluene (4.96 mL), triethylvinylgermane (0.644 g, 3.45 mmol), and hexene (0.871 g, 10.35 mmol) were placed in a 15 mL glass ampoule. The ampoule was closed and heated under argon at 100 °C for 24 h. The final product (contained 37 % of the *E* isomer) was separated from the residues of the catalyst and reactants by using a column of silica (eluent: hexane; $R_f=0.70$): ^1H NMR ($CDCl_3$): $\delta=6.61$ (d, 1H, $J_{H,H}=19.2$ Hz; Ge−HC=C*H*), 6.82 ppm (d, 2H, $J_{H,H}=19.2$ Hz; Ge−*H*C=CH).

(*E*/*Z*)-1-(Butoxy)-2-(triethylgermane)ethane (8a/b): [RuH(Cl)(CO)-(PCy_3)$_2$] (**I**) complex (50 mg, 0.068 mmol), toluene (6.26 mL), triethylvinylgermane (0.644 g, 3.45 mmol), and vinyl-*n*-butyl ether (3.46 g, 34.50 mmol) were placed in a 15-mL glass ampoule. The ampoule heated under argon at 65 °C for 24 h. The final product was separated from residues of the catalyst and reactants by using a column of silica (eluent: hexane/diethyl ether (3:1); $R_f=0.75$) to afford a mixture of **8a** and **8b** (0.75 g, 2.90 mmol, 84 % isolated yield, *E*/*Z* 65:35) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta=0.71$–0.81 (2t, 6H, $C\mathit{H}_3$, from *E*/*Z* isomers), 0.83–0.91 (2q, 4H; $CH_3-C\mathit{H}_2-Ge$, from *E*/*Z* isomers), 0.92–1.04 (2t, 6H; $C\mathit{H}_3-CH_2-Ge$, from *E*/*Z* isomers), 1.35–1.57 (m, 4H; $C\mathit{H}_2$, from *E*/*Z* isomers), 1.59–1.66 (m, 4H; $C\mathit{H}_2$, from *E*/*Z* isomers), 3.69–3.74 (2t, 4H; O−$C\mathit{H}_2$, from *E*/*Z* isomers), 4.24 (d, 1H, $J_{H,H}=7.8$ Hz; Ge−*H*C=CH, from *Z* isomer), 4.52 (d, 1H, $J_{H,H}=15.0$ Hz; Ge−*H*C=CH, from *E* isomer), 6.27 (d, 1H, $J_{H,H}=15.0$ Hz; HC=C*H*−O, from *E* isomer), 6.66 ppm (d, 1H, $J_{H,H}=7.8$ Hz; HC=C*H*−O, from *Z* isomer); ^{13}C NMR ($CDCl_3$): $\delta=4.85$ (Ge−CH_2, from *Z* isomer), 5.38 (Ge−CH_2, from *E* isomer), 8.96 ($\mathit{C}H_3-CH_2-Ge$, from *Z* isomer), 9.16 ($\mathit{C}H_3-CH_2-Ge$, from *E* isomer), 13.90 ($\mathit{C}H_3-CH_2$, from *Z* isomer), 13.98 ($\mathit{C}H_3-CH_2$, from *E* isomer), 19.14 ($CH_3-\mathit{C}H_2$, from *Z* isomer), 19.35 ($CH_3-\mathit{C}H_2$, from *E* isomer), 31.33 ($O-CH_2-\mathit{C}H_2$, from *Z* isomer), 32.01 ($O-CH_2-\mathit{C}H_2$, from *E* isomer), 67.51 ($O-\mathit{C}H_2-CH_2$, from *Z* isomer), 71.54 ($O-\mathit{C}H_2-CH_2$, from *E* isomer), 92.14 (=*C*H−Ge, from *Z* isomer), 96.91 (=*C*H−Ge, from *E* isomer), 153.91 (=*C*H−O, from *Z* isomer), 156.77 ppm (=*C*H−O, from *E* isomer); MS (EI): *m*/*z* (%) for *Z* isomer: 230 [$M^{+\cdot}-CH_2CH_3$] (76), 231 [$M^{+\cdot}-CH_2{=}CH_2$] (100), 205 [$M^{+\cdot}-CH_2{=}CH_2$] (42), 131 (31), 115 (7) 101 (14), 91 (6); *m*/*z* (%) for *E* isomer: 230 [$M^{+\cdot}-CH_2CH_3$] (46), 231 [$M^{+\cdot}-CH_2{=}CH_2$] (100), 205 [$M^{+\cdot}-CH_2{=}CH_2$] (61), 133 (38), 117 (9), 103 (17), 91 (9); elemental analysis calcd (%) for $C_{12}H_{26}GeO$: C 55.65, H 10.12; found: C 55.71, H 10.29.

(*E*)-9-[2-(Triethylgermyl)ethenyl]-9*H*-carbazole (9): [RuH(Cl)(CO)-(PCy_3)$_2$] (**I**) complex (42 mg, 0.058 mmol), toluene (5.24 mL), triethylvinylgermane (0.540 g, 2.89 mmol), and 9-carbazole (1.675 g, 8.67 mmol) were placed in a 15-mL glass ampoule. The ampoule was heated under argon at 110 °C for 24 h. The final product was separated from residues of the catalyst and reactants by using a column of silica (eluent: hexane/diethyl ether (4:1); $R_f=0.75$) to afford **9** (0.782 g, 2.22 mmol, 78 % isolated yield) as white crystals: ^1H NMR ($CDCl_3$): $\delta=0.90$ (q, 6H; $C\mathit{H}_2$), 1.06 (t, 9H; $C\mathit{H}_3$), 6.02 (d, 1H, $J_{H,H}=16.8$ Hz; Ge−*H*C=CH), 7.13 (d, 1H, $J_{H,H}=16.8$ Hz; HC=C*H*−N), 7.20 (m, 1H; =CH), 7.39 (t, 1H; =CH), 7.58 (d, 1H; =CH), 7.99 ppm (d, 1H, =CH); ^{13}C NMR ($CDCl_3$): $\delta=4.80$ (CH_2), 9.15 (CH_3), 110.43(=CH), 112.65 (=CH), 120.22 (=CH), 120.37(=CH), 123.77 (c_i), 126.02 (Ge−*C*H−CH), 132.52 (CH−*C*H−N), 139.17 ppm (c_i); MS (EI): *m*/*z* (%): 353 [$M^{+\cdot}$] (13), 325 [$M^{+\cdot}-CH_2{=}CH_2$] (100), 324 [$M^{+\cdot}-CH_3CH_2$] (35), 295 [$M^{+\cdot}-2\times CH_3CH_2$] (26), 265 (5); HRMS: calcd for $C_{20}H_{25}GeN$: 353.11988; found: 353.11972; elemental analysis calcd (%) for $C_{20}H_{25}GeN$: C 68.23, H 7.16, N, 3.98; found: C 69.03, H 7.30, N 4.11.

(*E*)-*N*-[2-(Triethylgermyn)ethenyl]pyrrolidinone (10): [RuH(Cl)(CO)-(PCy_3)$_2$] (**I**) complex (25 mg, 0.034 mmol), toluene (5.20 mL), triethylvinylgermane (0.644 g, 3.45 mmol), and 2-pyrrolidinone (1.151 g, 10.35 mmol) were placed in a 15-mL glass ampoule. The ampoule was heated under argon at 100 °C for 24 h. The final product was separated from residues of the catalyst and reactants by using a column of silica (eluent: hexane/diethylether (4:1); $R_f=0.75$) to afford **10** (0.773 g, 2.86 mmol, 83 % isolated yield) as a colorless liquid: ^1H NMR ($CDCl_3$): $\delta=0.80$ (q, 6H; CH_2), 1.02 (t, 9H; CH_3), 2.08 (m, 2H; CH_2), 2.51 (t, 2H; CH_2), 3.55 (t, 2H; CH_2), 4.84 (d, 1H, $J_{H,H}=17.4$ Hz; Ge−*H*C=CH), 7.02 ppm (d, 1H, $J_{H,H}=17.1$ Hz; HC=C*H*−N); ^{13}C NMR ($CDCl_3$): $\delta=4.69$ (CH_2), 8.98 (CH_3), 17.40 (CH_2), 44.70 (CH_2), 103.87 (Ge−*C*H=CH), 132.66 (CH=*C*H−N), 172.59 ppm (c_i); MS (EI): *m*/*z* (%): 243 [$M^{+\cdot}-CH_2{=}CH_2$] (100), 212 (6), 184 (8), 70 (5); HRMS: calcd for $C_{12}H_{23}GeNO$: 271.09914; found: 271.09965; elemental analysis calcd (%) for $C_{12}H_{23}GeNO$: C 53.39, H 8.59, N 5.19; found: C 53.59, H 8.70, N 5.27.

Trimethylvinylgermane (11): Chlorotrimethylgermane (5 g, 32.68 mmol) and dried and deoxidized tetrahydrofuran (THF; 30 mL) were placed in a Schlenk tube equipped with a magnetic stirrer under argon, then a solution of $CH_2{=}CHMgBr$ in THF (20.50 mL, 1.6 mol L^{-1}) was added dropwise. (The vinylmagnesium bromide was synthesized according to the procedure described in the literature.[14]) The reaction was left for 3 h at room temperature with stirring. After this time, the reaction mixture was washed with water three times and dried over $CaCl_2$. The trimethylvinyl germane was purified by trap-to-trap distillation (75 % yield): ^1H NMR ($CDCl_3$): $\delta=0.19$ (s, 9H; CH_3), 5.62 (dd, 1H; $Ge-CH{=}C\mathit{H}_2$), 5.94 (dd, 1H; $Ge-CH{=}C\mathit{H}_2$), 6.34 ppm (dd, 1H; $Ge-C\mathit{H}{=}CH_2$); ^{13}C NMR ($CDCl_3$): $\delta=1.93$ (CH_3), 129.385 ($Ge-HC{=}\mathit{C}H_2$), 141.02 ppm ($Ge-H\mathit{C}{=}CH_2$).

Triethylvinylgermane (12): Compound **12** was prepared from the appropriate starting materials according to the above procedure for **11** (66 % yield): ^1H NMR ($CDCl_3$): $\delta=0.77$ (q, 6H; CH_2) 1.03 (t, 9H; CH_3), 5,64 (dd, 1H; $CH{=}C\mathit{H}_2$), 6.03 (dd, 1H; $CH{=}C\mathit{H}_2$), 6.28 ppm (dd, 1H; $Ge-C\mathit{H}{=}CH_2$); ^{13}C NMR ($CDCl_3$): $\delta=4.37$ ($\mathit{C}H_2$), 9.110 (CH_3), 130.94 ($Ge-HC{=}\mathit{C}H_2$), 137.49 ppm ($Ge-H\mathit{C}{=}CH_2$); MS (EI): *m*/*z* (%): 188 [$M^{+\cdot}$] (1), 159 [$M^{+\cdot}-CH_2CH_3$] (100), 131 (72), 101 (39), 75 (11); HRMS: calcd for $C_8H_{18}Ge$: 188.06203; found 188.06201.

Synthesis of [Ru(Cl)(GeMe$_3$)(CO)(PPh$_3$)$_2$] (III): The complex [RuH(Cl)(CO)(PPh_3)$_3$] (**II**; 0.373 g, 0.392 mmol) and toluene (6.27 mL) were placed into a 50-mL Schlenk flask equipped with a magnetic stirrer, where they formed a suspension. Subsequently, $H_2C{=}CHGeMe_3$ (0.334 mL, 1.961 mmol) was added to the mixture, which was then warmed at 80 °C and stirred for an additional 24 h. After that, the final mixture was cooled at room temperature, provisionally purified by using a "canula with drain" system, and transported to the next Schlenk tube. The excess solvent was evaporated under reduced pressure and pentane (35 mL) was added to give a yellow precipitate. Later, the pentane was decanted and the new complex was washed twice with cold pentane (2× 15 mL). The yellow solid was dried under vacuum (0.284 g, 90 % yield): m.p. = 219–221 °C (decomp.); ^1H NMR (C_6D_6): $\delta=0.70$ (s, 9H; Ge-(CH_3)$_3$), 7.05 (m, 15H; C_6H_5), 7.85 ppm (m, 15H; C_6H_5); ^{13}C NMR (C_6D_6): $\delta=10.17$ (CH_3), 128.17 (*m*-C_6H_5), 130.05 (*p*-C_6H_5), 132.68 (c_i-C_6H_5), 134.60 (*o*-C_6H_5), 200.09 ppm (CO); ^{31}P NMR (C_6D_6): $\delta=34.59$ ppm (s, 2PPh); elemental analysis calcd for $C_{40}H_{39}ClGeOP_2Ru$: C 59.55, H 4.87; found: C 60.24, H 4.92. Single crystals of **III** suitable for an X-ray crystal structure analysis were obtained by recrystallization from toluene at 0 °C for 24 h.

Experimental data of X-ray analysis: Diffraction data were collected at room temperature by the ω-scan technique up to $2\theta=60°$ (836 frames) on a KUMA-KM4CCD diffractometer[15] with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz polarization effects[16] as well as for absorption by SORTAV.[17] Accurate unit-cell parameters were determined by the least-squares fit of 9448 reflections of highest intensity, chosen from the whole experiment. The structures were solved with the SHELXS97 software[18] and refined with the full-matrix least-squares procedure on F^2 with the SHELXL97 program.[19] Scattering factors incorporated in the SHELXL97 program[20] were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + 0.0262 \times P^2]$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups; the U_{iso} values of hydrogen atoms were set at 1.2 (1.3 for methyl groups) times the U_{eq} value of the appropriate carrier atom. The chlorine and carbonyl groups were found disordered over two positions with s.o.f. values of 0.5. Their positions and anisotropic thermal parameters were successfully refined with weak restraints applied to the thermal parameters of one of the carbonyl groups.

X-ray crystal structure analysis: The trimethylgermyl group ($Ge(CH_3)_3$) has only slightly distorted tetrahedral geometry (mean value of the C−Ge−C angle is 104.7° and of the Ge−Ru−C angle is 113.8°). Similar geometry was observed in $[Ru(CO)(Cl)(SiMe_3)(PPh_3)_2]$,[21b] while a significantly larger distortion was reported in the trichlorosilyl group in $[Cp(PMe_3)_2Ru(SiCl_3)]$[22] The bond lengths are typical; however, the [Ru−Ge] bond length of 2.4455(4) Å is one of the shortest found so far.

Selected bond lengths [Å] and angles [°] for III: Ru(1)−C(1) 1.723(6), Ru(1)−C(2) 1.786(9), Ru(1)−Cl(1) 2.466(3), Ru(1)−Cl(2) 2.480(3), Ru(1)−P(2) 2.3686(6), Ru(1)−P(3) 2.3921(6), Ru(1)−Ge(1) 2.4455(4), Ge(1)−C(12) 1.954(3), Ge(1)−C(13) 1.960(3), Ge(1)−C(11) 1.981(4), P(2)−C(231) 1.828(3), P(2)−C(211) 1.839(2), P(2)−C(221) 1.846(3), P(3)−C(331) 1.829(3), P(3)−C(321) 1.832(2), P(3)−C(311) 1.838(2), C(1)−O(1) 1.215(7), C(2)−O(2) 1.003(10); C(1)-Ru(1)-P(2) 88.24(17), C(2)-Ru(1)-P(2) 91.5(2), C(1)-Ru(1)-P(3) 91.17(17), C(2)-Ru(1)-P(3) 90.3(2), C(1)-Ru(1)-Ge(1) 86.4(2), C(2)-Ru(1)-Ge(1) 90.3(3), P(2)-Ru(1)-P(3) 160.51(2), P(2)-Ru(1)-Ge(1) 101.120(18), P(3)-Ru(1)-Ge(1) 98.278(18), C(1)-Ru(1)-Cl(1) 170.5(2), P(2)-Ru(1)-Cl(1) 88.65(6), P(3)-Ru(1)-Cl(1) 88.78(6), Ge(1)-Ru(1)-Cl(1) 103.01(6), C(2)-Ru(1)-Cl(2) 171.9(3), P(2)-Ru(1)-Cl(2) 86.71(5), P(3)-Ru(1)-Cl(2) 88.87(5), Ge(1)-Ru(1)-Cl(2) 97.79(6), C(12)-Ge(1)-C(13) 102.72(16), C(12)-Ge(1)-C(11) 106.7(2), C(13)-Ge(1)-C(11) 104.86(16), C(12)-Ge(1)-Ru(1) 113.79(11), C(13)-Ge(1)-Ru(1) 114.76(11), C(11)-Ge(1)-Ru(1) 113.03(13), C(231)-P(2)-C(211) 106.18(12), C(231)-P(2)-C(221) 102.19(11), C(211)-P(2)-C(221) 101.34(11), C(231)-P(2)-Ru(1) 97.28(8), C(211)-P(2)-Ru(1) 121.16(9), C(221)-P(2)-Ru(1) 125.45(8), C(212)-C(211)-P(2) 118.4(2), C(216)-C(211)-P(2) 123.4(2), C(222)-C(221)-P(2) 122.2(2), C(226)-C(221)-P(2) 119.8(2), C(232)-C(231)-P(2) 119.95(19), C(236)-C(231)-P(2) 121.4(2), C(331)-P(3)-C(321) 103.18(11), C(331)-P(3)-C(311) 103.23(11), C(321)-P(3)-C(311) 102.77(11), C(331)-P(3)-Ru(1) 106.17(8), C(321)-P(3)-Ru(1) 116.10(8), C(311)-P(3)-Ru(1) 123.07(8), C(312)-C(311)-P(3) 123.0(2), C(316)-C(311)-P(3) 119.1(2), C(322)-C(321)-P(3) 123.9(2), C(326)-C(321)-P(3) 118.47(19), C(332)-C(331)-P(3) 118.49(18), C(336)-C(331)-P(3) 123.2(2), O(1)-C(1)-Ru(1) 176.6(6), O(2)-C(2)-Ru(1) 177.9(13).

X-ray crystal structure data: In the Cambridge Crystallographic Database[23] there are only 14 compounds with the Ru−Ge bond and only one with a trimethylgermyl group (this compound is also the only five-coordinated ruthenium in this group): dimeric μ_2-pentalene-bis(dicarbonyl(trimethylgermyl)-ruthenium).[24] In total, there are only eight structures of metal complexes with trimethylgermyl group.

Relevant crystal data are listed in Table 2, together with refinement details.

CCDC-262997 contains 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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Table 2. Crystal data and structure refinement for **III**.

empirical formula	$C_{40}H_{39}ClGeOP_2Ru$
formula weight	806.76
T [K]	293(2)
wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$
unit-cell dimensions:	
a [Å]	11.6930(5)
b [Å]	18.8381(8)
c [Å]	17.0402(7)
β [°]	96.150(3)
volume [Å^3]	3731.9(3)
Z	4
ρ_{calcd} [$mg\,m^{-3}$]	1.436
μ [mm^{-1}]	1.397
$F(000)$	1640
crystal size [mm^3]	$0.2 \times 0.3 \times 0.3$
θ range for data collection [°]	4.85–29.89
index ranges	$-16 \leq h \leq 15$ $0 \leq k \leq 26$ $0 \leq l \leq 23$
reflections collected	36609
independent reflections (R(int))	9761 (0.048)
completeness to $\theta = 25.00°$ [%]	99.0
goodness-of-fit on F^2	0.913
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0356$, $wR2 = 0.0637$
R indices (all data)	$R1 = 0.0662$, $wR2 = 0.0697$
largest diff. peak and hole [e Å^{-3}]	1.030 and −1.063

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