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Dipyrromethane-Based PGeP Pincer Germyl Rhodium Complexes

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Abstract: A family of germyl rhodium complexes derived from the PGeP germylene 2,2′-bis(di-isopropylphosphanylmethyl)-5,5′-dimethyldipyrromethane-1,1′-diylgermanium(II), $Ge(pyrmP^{i}Pr_2)_2CMe_2$ (**1**), has been prepared. Germylene **1** reacted readily with $[RhCl(PPh_3)_3]$ and [RhCl(cod)(PPh$_3$)] (cod = 1,5-cyclooctadiene) to give, in both cases, the PGeP-pincer chloridogermyl rhodium(I) derivative $[Rh\{\kappa^3P,Ge,P\text{-}GeCl(pyrmP^{i}Pr_2)_2CMe_2\}(PPh_3)]$ (**2**). Similarly, the reaction of **1** with [RhCl(cod)(MeCN)] afforded $[Rh\{\kappa^3P,Ge,P\text{-}GeCl(pyrmP^{i}Pr_2)_2CMe_2\}(MeCN)]$ (**3**). The methoxidogermyl and methylgermyl rhodium(I) complexes $[Rh\{\kappa^3P,Ge,P\text{-}GeR(pyrmP^{i}Pr_2)_2CMe_2\}(PPh_3)]$ (R = OMe, **4**; Me, **5**) were prepared by treating complex **2** with LiOMe and LiMe, respectively. Complex **5** readily reacted with CO to give the carbonyl rhodium(I) derivative $[Rh\{\kappa^3P,Ge,P\text{-}GeR(pyrmP^{i}Pr_2)_2CMe_2\}(CO)]$ (**6**), with HCl, $HSnPh_3$ and Ph_2S_2 rendering the pentacoordinate methylgermyl rhodium(III) complexes $[RhHX\{\kappa^3P,Ge,P\text{-}GeMe(pyrmP^{i}Pr_2)_2CMe_2\}]$ (X = Cl, **7**; $SnPh_3$, **8**) and $[Rh(SPh)_2\{\kappa^3P,Ge,P\text{-}GeMe(pyrmP^{i}Pr_2)_2CMe_2\}]$ (**9**), respectively, and with H_2 to give the hexacoordinate derivative $[RhH_2\{\kappa^3P,Ge,P\text{-}GeMe(pyrmP^{i}Pr_2)_2CMe_2\}(PPh_3)]$ (**10**). Complexes **3** and **5** are catalyst precursors for the hydroboration of styrene, 4-vinyltoluene and 4-vinylfluorobenzene with catecholborane under mild conditions.

Introduction

Pincer complexes containing heavier tetrylenes (silylenes, germylenes, stannylenes; HTs) as ligands combine two features that have important implications in the catalytic activity of these complexes. On one hand, the tridentate coordination of pincer ligands enhances the stability of the complexes and their ease steric and electronic tunability help establish the tricky balance between reactivity and stability often required by catalytically efficient metal complexes.[1,2] On the other hand, many HTs have shown a very strong electron-donating character, with a basicity often greater than that of N-heterocyclic carbenes,[3] and strong electron-donating ligands are frequently required by catalytically active complexes to promote oxidative addition processes.[4] Consequently, many transition metal (TM) complexes containing HT ligands have already been identified as active homogeneous catalysts.[3c,5–8] It is noteworthy that cooperativity between the tetrel atom and the TM (both participate in catalytic steps) has been observed in some occasions.[6a,8] However, metal complexes comprising an HT as part of a pincer ligand are still limited to ECE,[6] ENE,[7] PEP[9,10a,b,11–16] and SES[10c,d] pincer platforms (E = Si, Ge or Sn).

Regarding metal-free PGeP pincer-type germylenes,[17] we reported the first one in 2017 (compound **A**, Figure 1)[11] and also the synthesis of some d^8 metal (Rh, Ir, Ni, Pd, Pt) derivatives,[18] but the small 5-membered Ge-containing ring and the short length of its $CH_2P^tBu_2$ sidearms resulted in very distorted square geometries. Goicoechea's group reported the second PGeP germylene (compound **B**, Figure 1), but it did not behave as a pincer ligand because its small 5-membered GeN_2C_2 ring forces a long separation between the P atoms, hampering their binding to the same metal atom.[12] A more flexible ligand framework was presented by germylene **C** (Figure 1), but the little steric protection of its Ge atom resulted

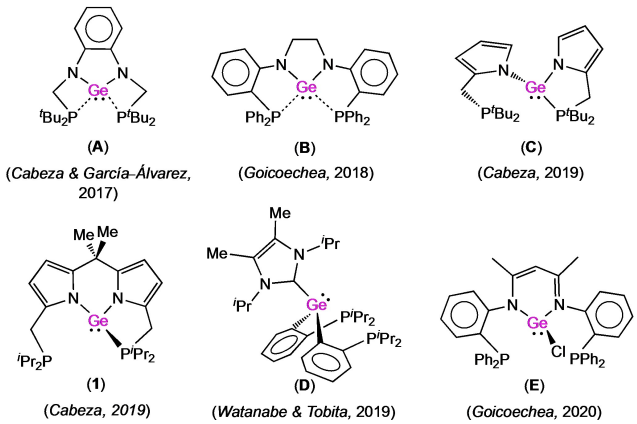

Figure 1. The currently known metal-free PGeP germylenes.

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in low stability of its TM derivatives.[13] Aiming at obtaining more stable PGeP complexes, we have recently synthesized germylene **1** (Figure 1),[14] which is based on the dipyrromethane scaffold, and we have already demonstrated that it is well suited to form unstrained square planar (Fe^{II},[19] Co^{II},[19] Ni^{II},[19,20] Pd^{II}[20]), tetrahedral (Cu^{I},[14,19] Zn^{II}[19]) and T-shaped tricoordinate (Pd^{0},[21] Ag^{I},[14] Au^{I}[14]) complexes, most of them being chloridogermyl-metal derivatives. Although two additional metal-free PGeP germylenes have also been reported, **D** and **E** (Figure 1), the former has only been used to prepare nickel(0) complexes,[15] whereas no reaction of the latter with a TM complex has as yet been reported.[22]

We now report the first rhodium(I) and rhodium(III) complexes derived from germylene **1**, including the first ones in which the metal is penta- and hexacoordinated. Additionally, this paper also describes the first catalytic study (olefin hydroboration) involving a transition metal derivative of germylene **1**.

Results and Discussion

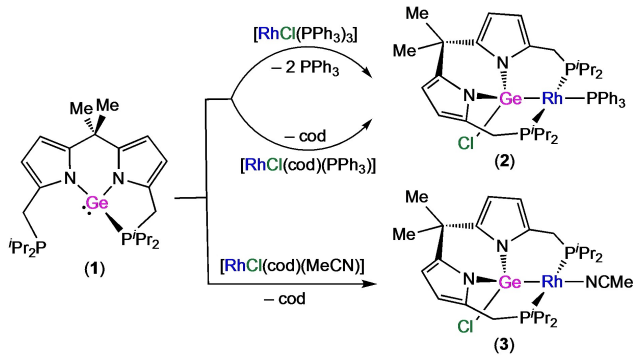
Germylene **1** reacted with $[RhCl(PPh_3)_3]$, in toluene at room temperature, to give $[Rh\{\kappa^3P,Ge,P\text{-}GeCl(pyrmP^iPr_2)_2CMe_2\}(PPh_3)]$ (**2**) as the only reaction product (Scheme 1). However, extensive washing with hexane was necessary to separate it from the released PPh_3, lowering the yield of isolated product to 74%. Alternatively, complex **2** was also prepared in greater yield (95%) by treating germylene **1** with $[RhCl(cod)(PPh_3)]$ (cod = 1,5-cyclooctadiene) (Scheme 1). The presence of one PPh_3 ligand and the C_S symmetry of the complex were confirmed by its NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum showed two signals, doublet of doublets and doublet of triplets, due to $J_{P\text{-}Rh}$ and $J_{P\text{-}P'}$ couplings, while the ^1H NMR spectrum showed diastereotopic protons for the CH_2 and P^iPr_2 groups, also indicating that the CMe_2 methyl groups are located in the symmetry plane.

Therefore, the syntheses of complex **2** implies the displacement of neutral ancillary ligands (PPh_3 or cod) and the insertion of the Ge atom of germylene **1** into the M–Cl bond of the corresponding starting chlorido metal complex. Although this type of reactivity has been previously observed for other PGeP germylenes in their reactions with metal complexes,[17,19] the maintenance of one PPh_3 ligand attached to the metal atom was surprising because: a) the reactions of germylene **1** with $[MCl(PPh_3)]$ (M = Ag, Au) and $[Pd(PPh_3)_4]$ lead to the coordinatively unsaturated T-shaped metal complexes $[M\{\kappa^3P,Ge,P\text{-}GeCl(pyrmP^iPr_2)_2CMe_2\}]$ (M = Ag, Au)[14] and $[Pd\{\kappa^3P,Ge,P\text{-}Ge(pyrmP^iPr_2)_2CMe_2\}]$,[21] which do not contain PPh_3 and have the metal atom sterically protected by the P^iPr_2 groups, and b) all the currently known square planar complexes derived from germylene **1** have a small ligand (H, Cl or SPh) in the position occupied by the PPh_3 ligand in complex **2** (*trans* to the Ge atom).[19,21]

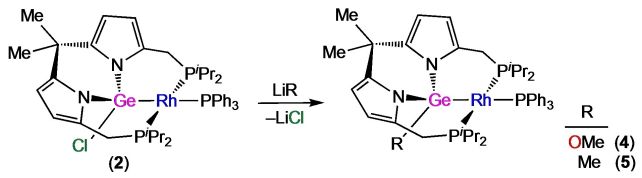
Our purpose to involve some rhodium derivatives of germylene **1** in catalytic reactions (see below) and the above-described efficient preparation of **2** from $[RhCl(cod)(PPh_3)]$ led us to investigate the reaction of **1** with [RhCl(cod)(MeCN)], because acetonitrile frequently behaves as a labile ligand and this feature is often required by catalytically active complexes. The acetonitrile derivative $[Rh\{\kappa^3P,Ge,P\text{-}GeCl(pyrmP^iPr_2)_2CMe_2\}(MeCN)]$ (**3**) (Scheme 1) was satisfactorily prepared (83% yield) using this synthetic method. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **3** confirmed the presence of acetonitrile in the complex and that the molecule also has C_S symmetry.

Both complexes, **2** and **3**, proved to be very sensitive to moisture, leading to mixtures when exposed to wet solvents. Aiming at preparing complexes with lower tendency to undergo hydrolysis, we treated complex **2** with LiOMe and LiMe to replace the Cl atom of the GeCl fragment by OMe and Me groups, respectively. These reactions led to complexes $[Rh\{\kappa^3P,Ge,P\text{-}GeR(pyrmP^iPr_2)_2CMe_2\}(PPh_3)]$ (R = OMe, **4**; Me, **5**) (Scheme 2). Analogous reactions were attempted with complex **3** but they gave inseparable mixtures.[23]

The NMR spectra of **4** and **5** were comparable to those of complex **2**, but the ^1H and $^{13}C\{^1H\}$ NMR spectra additionally showed the presence of the OMe or Me groups, as appropriate. The molecular structure of the methoxidogermyl complex **4** was determined by X-ray diffraction (XRD) (Figure 2). Interestingly, the Rh-PPh_3 distance, 2.3505(7) Å, is unusually long (for comparison, that of $[RhCl(CO)(PPh_3)_2]$ is 2.322(1) Å[24]), being longer than the Rh-P^iPr_2 distances, 2.3352(7) and 2.3281(7) Å. Although the positions of the P^iPr_2 methyl groups minimize the steric repulsion between the PPh_3 phenyl and P^iPr_2 isopropyl groups in complex **4**, the steric hindrance between the PPh_3 phenyl and P^iPr_2 isopropyl Me_2CH groups is claimed as responsible for the long Rh–P distances found for this complex (space-filling diagrams are shown in the Supporting Information, Figure S29).



Scheme 1. Syntheses of complexes **2** and **3**.



Scheme 2. Synthesis of complexes **4** and **5**.

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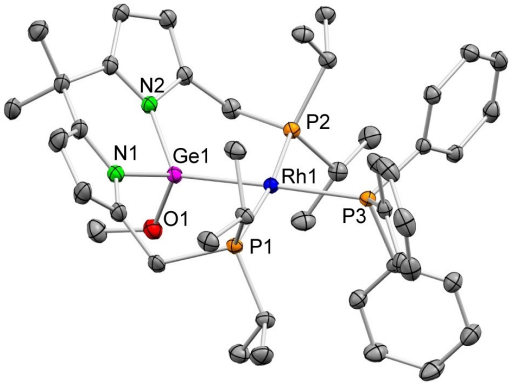
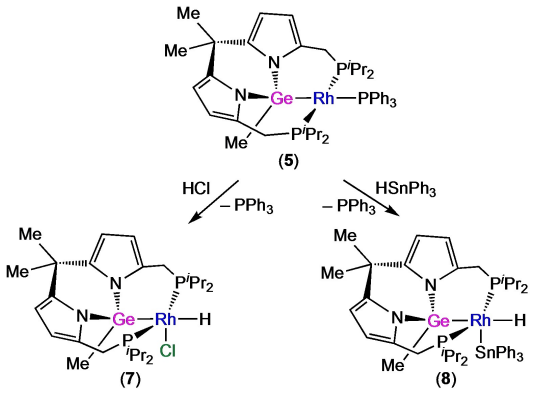


Figure 2. Thermal ellipsoid diagram of the XRD molecular structure of complex **4** (40% displacement ellipsoids, H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Rh1-P1 2.3352(7), Rh1-P2 2.3281(7), Rh1-P3 2.3505(7), Rh1-Ge1 2.3540(4), Ge1-O1 1.811(2), Ge1-N1 1.901(2), Ge1-N2 1.892(2); N1-Ge1-N2 92.6(1), N1-Ge1-Rh1 119.90(7), N2-Ge1-Rh1 119.83(7), N1-Ge1-O1 105.2(1), N2-Ge1-O1 104.5(1), O1-Ge1-Rh1 112.15(7), Ge1-Rh1-P1 84.78(2), P1-Rh1-P2 168.81(3), P1-Rh1-Ge1 84.78(2), P2-Rh1-Ge1 85.21(2), P1-Rh1-P3 94.76(3), P2-Pd1-P3 95.10(3).



Scheme 4. Synthesis of complexes **7** and **8**.

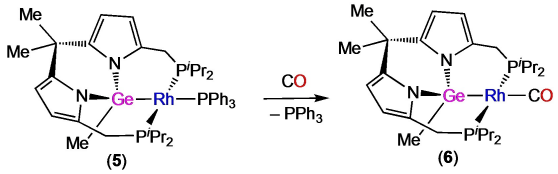
The stability of the methylgermyl complex **5** toward hydrolysis led us to choose it for a reactivity study. The lability of its PPh_3 ligand was first evidenced by its reaction with carbon monoxide (gas bubbled in toluene at room temperature), which immediately gave the carbonyl derivative [Rh{κ³*P*,Ge,*P*-GeMe(pyrmP^{i}Pr$_2$)$_2$CMe$_2$}(CO)] (**6**; Scheme 3), characterized by a strong ν_{CO} absorption at 1967 cm^{-1} in its IR spectrum (toluene solution). The low frequency of this absorption is indicative of a high electron-richness of the metal center (strong π-back-bonding to the CO ligand).

As the metal atom of the triphenylphosphane complex **5** should be even more electron-rich than that of the carbonyl derivative **6** (CO is more π-acceptor than PPh_3) and given the proven lability of its PPh_3 ligand, we decided to use complex **5** to investigate oxidative addition reactions because not a single example of a rhodium(III) complex supported by a PGeP pincer ligand had previously been reported.

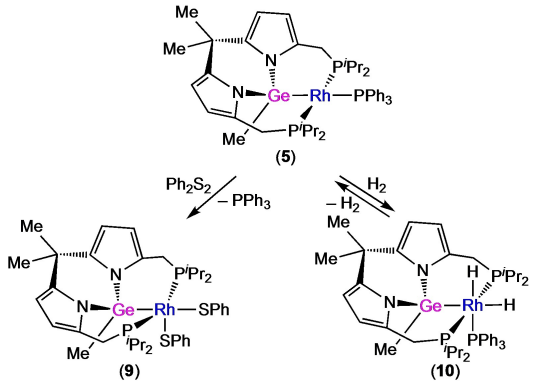
Complex **5** reacted readily with one equivalent of HCl (ethereal solution) and $HSnPh_3$ to give the rhodium(III) complexes [RhHX{κ³*P*,Ge,*P*-GeMe(pyrmP^{i}Pr$_2$)$_2$CMe$_2$}] (X = Cl, **7**; $SnPh_3$, **8**) (Scheme 4). Both compounds showed a highly shielded hydride resonance in their ^{1}H NMR spectra (C_6D_6), at δ −26.3 ppm (dt, $J_{H\text{-}Rh}$ = 36.0 Hz, $J_{H\text{-}P}$ = 13.5 Hz) for **7** and −28.4 ppm (br) for **8**, and just one signal (doublet, due to *J* ^{31}P-^{103}Rh coupling) in their ^{31}P{^{1}H} NMR spectra (tin satellites were also showed in the spectrum of **8**). A doublet of triplets ($J_{Sn\text{-}Rh}$ = 336 Hz, $J_{Sn\text{-}P}$ = 180 Hz) was observed in the ^{119}Sn{^{1}H} NMR spectrum (C_6D_6) of **8**. Therefore, compounds **7** and **8** do not contain the PPh_3 ligand of their starting reagent (**5**) and are coordinatively unsaturated pentacoordinated rhodium(III) complexes, the first ones to contain a PGeP pincer ligand. The oxidative addition of HX molecules to rhodium(I) pincer complexes has been previously reported; however, the products are hexacoordinate species in most cases.[25]

We wanted to check whether two ligands different from (and larger than) hydride could be accommodated on the rhodium atom despite the great steric shielding exerted by the P^{i}Pr$_2$ groups. With that purpose, we chose diphenyldisulfide because the oxidative addition of its S–S bond to low-valent metal complexes had been previously reported to proceed cleanly under mild conditions.[21] The reaction of complex **5** with diphenyldisulfide proceeded quickly in toluene at room temperature, to give the pentacoordinate rhodium(III) complex [Rh(SPh)$_2${κ³*P*,Ge,*P*-GeMe(pyrmP^{i}Pr$_2$)$_2$CMe$_2$}] (**9**) (Scheme 5). Again, the PPh_3 ligand of **5** was released during this reaction.

Complex **5** also reacted with hydrogen under mild conditions (gas bubbled, C_6D_6 solution, room temperature, J. Young-stopped NMR tube) to give [RhH$_2${κ³*P*,Ge,*P*-GeMe(pyrmP^{i}Pr$_2$)$_2$CMe$_2$}(PPh$_3$)] (**10**) (Scheme 5) in quantitative



Scheme 3. Synthesis of complex **6**.



Scheme 5. Synthesis of complexes **9** and **10**.

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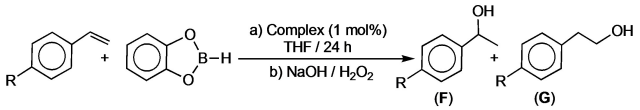
yield. Its NMR spectra confirmed the presence of two hydride ligands, observed as two broad resonances in the ^{1}H spectrum, one of them showing a strong coupling to a P atom ($J_{H\text{-}P}$ = 140 Hz), indicating a *trans* hydride-P arrangement, and the maintenance of the PPh_3 ligand, observed as a doublet of triplets in the $^{31}P\{^{1}H\}$ NMR spectrum (the latter also contained the doublet of doublets expected for the $P^{i}Pr_2$ groups). Therefore, compound **10** is a hexacoordinate derivative, the first one ever reported for a PGeP pincer rhodium(III) complex. Unfortunately, probably due to the steric hindrance exerted by the $P^{i}Pr_2$ groups, complex **10** could not be isolated as a pure solid because, in the absence of a dihydrogen atmosphere, it slowly released dihydrogen in solution at room temperature, reverting to complex **5**.

Complexes **5** and **3** were tested as catalyst precursors for the hydroboration of styrenes with catecholborane (Table 1).[26] The reactions were carried out in dry THF, under argon (glove box), using equimolar amounts of the borane and the corresponding styrene and a 1 mol% of rhodium complex. After 24 h at room temperature, the reaction mixtures were oxidatively hydrolyzed with hydrogen peroxide and NaOH to give mixtures of the corresponding branched (**F**) and terminal (**G**) alcohols that were analyzed by GC and NMR after a conventional workup.

Table 1 shows that the acetonitrile complex **3** is only a bit more active than the triphenylphosphane complex **5**. However, while the activity and regioselectivity of **5** (entry 1) are similar to those found for other phosphane derivatives of rhodium, which preferentially afford the branched alcohol,[26,27] the selectivity of **3** was the opposite, preferentially giving the terminal alcohol (entry 2). Linear-selective hydroboration[28] is unusual for precious-metal catalysts. The catalytic activity of complex **3** decreased for ring-substituted styrenes, regardless of the electron-donating (entry 3) or -withdrawing (entry 4) character of the substituent, indicating that the kinetics of these reactions strongly depends on the volume of the substrate. Aiming at shedding some light on the mechanism of the hydroboration reaction, complex **3** was individually treated with styrene and catecholborane at room temperature, but styrene did not react and catecholborane led to a mixture that could not be separated and identified.

These catalytic results, although of moderate interest as far as activity and selectivity are concerned, are the first ones to be reported for a transition metal derivative of germylene **1**. Only a few metal complexes containing other PGeP germyl ligands have been previously involved in other catalytic reactions.[29]

Table 1. Catalytic hydroboration of styrenes promoted by complexes **5** and **3**.



Entry	Complex	R	Conversion [%]	**F**/**G** ratio [%]
1	**5**	H	87	62/38
2	**3**	H	94	24/76
3	**3**	Me	29	25/75
4	**3**	F	36	25/75

Conclusions

The reactions of germylene **1** with a series rhodium(I) chlorido complexes afforded in all cases reaction products (**2**, **3**) that contain a PGeP pincer chloridogermyl ligand that arises from the insertion of the divalent Ge atom of germylene **1** into the Rh–Cl bond. The Cl atom of the chloridogermyl group of complex **2** has been replaced by OMe and Me groups (**4**, **5**). The lability of the PPh_3 ligand of complex **5** has allowed a rich derivative chemistry that has afforded carbonyl rhodium(I) (**6**) and oxidative addition rhodium(III) reaction products (**7**–**10**), through processes that proceeded quickly with release of PPh_3. While tri-[14,21] and tetra-coordinate[14,19–21] PGeP pincer germyl metal complexes derived from germylene **1** have been previously reported, the reactions described in this manuscript widen the scope of metal geometries that can be supported by ligands of this type, as they have afforded unprecedented penta- (**7**–**9**) and hexa-coordinate (**10**) metal complexes. We have also shown that complexes **3** and **5** promote the hydroboration of styrenes under mild conditions.

The results reported in this article demonstrate that the PGeP pincer germyl ligands derived from germylene **1** are very versatile, as they can stabilize a wide range of metal coordination types while they sterically protect the metal atom with the $P^{i}Pr_2$ groups. This work broadens two currently very active research areas within the fields of coordination and organometallic chemistries: pincer ligands[1,2,17] and heavier tetrel element-donor ligands.[30]

Experimental Section

Detailed synthetic procedures and analytical, spectroscopic and structural (XRD) data for compounds **1**–**10** are given in the Supporting Information. Deposition Number 2157524 (for **4**·C_7H_8) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: germylenes · hydroboration · PGeP pincers · pincer complexes · rhodium

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