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From Bis(silylene) and Bis(germylene) Pincer-Type Nickel(II) Complexes to Isolable Intermediates of the Nickel-Catalyzed Sonogashira Cross-Coupling Reaction

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ABSTRACT: The first [ECE]Ni(II) pincer complexes with $E = Si^{II}$ and $E = Ge^{II}$ metallylene donor arms were synthesized via C-X (X = H, Br) oxidative addition, starting from the corresponding [EC(X)E] ligands. These novel complexes were fully characterized (NMR, MS, and XRD) and used as catalyst for Ni-catalyzed Sonogashira reactions; these catalysts allowed detailed information on the elementary steps of this catalytic reaction (transmetallation→oxidative addition→reductive elimination), resulting in the isolation and characterization of an unexpected intermediate in the transmetallation step. This complex, {[ECE]Ni-acetylide→CuBr} contains both nickel and copper, with the copper bound to the alkyne π -system. Consistent with these unusual structural features, DFT calculations of the {[ECE]Niacetylide→CuBr} intermediates revealed an unusual E-Cu-Ni three-center-two-electron bonding scheme. The results reveal a general reaction mechanism for the Ni-based Sonogashira coupling and broaden the application of metallylenes as strong σ -donor ligands for catalytic transformations.

INTRODUCTION

Transition metal (TM) centers create a vast range of applications in organometallic chemistry, but the ligands control the reactivity of these sites. During the last decades, many ligands have been developed that have created a wide range of new reactivities. For example, the pincer-type motif [EDE], a tridentate, meridional coordinating ligand framework offers a myriad of opportunities to fine-tune the steric and electronic properties of TM complexes.¹

Generally, the arms (E) of a pincer ligand consist of neutral, two-electron Lewis donor moieties (e.g. $E = PR_2$, NR_2 , or SR), which are connected over a linker group (often CH_2 or O) to the neutral or mono-anionic anchoring site (D; e.g. a pyridyl or phenyl group). Highly electron-rich [PCP] pincer complexes of Ir have been applied to activate the strong bonds of ammonia² and alkanes,³ and [PCP]Pd systems catalyze C-C coupling reactions.⁴

 σ -Stabilized metallylene (silylene or germylene) donor ligands also have given rise to unique properties and reactivities.^{5,6} It is noteworthy that bis-silylene and -germylene pincer moieties are more σ–donating than P^{III}-based ligands. This difference in σ donation was established through structural and spectroscopic investigation of the series of iridium olefin [ECE]IrHCl(coe) (E = Si, Ge, P) complexes.⁷ In addition, the first experiments with the bis-silylene pincer arene **SiCHSi** and the group 10 metal precursor Pd(PPh₃)₄ led to the unexpected formation of a mixed silylene(Si^{II})-

silyl(Si^{IV})-pincer Pd(II) complex (Scheme 1).⁸ This unexpected result raised the question of whether isolable group 10 metal [ECE]M(II)X complexes (E = Si^{II}, Ge^{II}; X = halogen) with E: \rightarrow M(II) \leftarrow :E coordination are at all accessible.

Scheme 1. Earlier and present complexation studies of ECXE pincer ligands toward group 10 metals.



On the other hand, cross coupling reactions are one of the most important breakthroughs in chemical synthesis.^{9,10} Although, the catalytic pathways remain unclear and in rare cases reaction intermediates have been isolated.^{9e,10b,f} Lately the Sonogashira reaction, normally catalyzed by Pd^o species with CuI as cocatalyst (Figure 1), has been catalyzed using nickel-based catalysts.^{10g,h} Nickel pincer complexes were recently reported to catalyze Sonogashira reactions¹⁰ between a terminal alkyne and a sp² (or sp³)¹¹ hybridized carbon electrophile (typically in the presence of a copper cocatalyst). The authors of the later work proposed that the catalytic cycle might involve a Ni^{II} \rightarrow Ni^{IV} couple, but no experimental evidence for the formation of Ni^{IV} was gained. Therefore, it is important to gain access to intermediates that could reveal the connections between the structures of the intermediates and the rates and selectivity of the intermediates.



Figure 1. General conditions in Sonogashira cross coupling.

Herein, we report the synthesis of the novel bromo bis-germylene **GeCBrGe** pincer arene and the straightforward coordination chemistry of the **ECHE** (E = Si, Ge) and **GeCBrGe** ligands towards nickel, a non-precious metal center. These studies led to the formation of [ECE]NiBr complexes, and these complexes catalyzed the Sonogashira coupling reaction (Scheme 1). Most important, reactions catalyzed by these strong σ -donor based pincer ligands enabled the isolation of elusive intermediates of the Sonogashira coupling. The results demonstrate for the first time, that chemical transformations at a non-precious metal center with pincer-like metallylene donor arms are viable processes.

RESULTS AND DISCUSSION

Synthesis of the GeCBrGe pincer ligand. From our previous metallation studies on the **SiCHSi** ligand with a group 10 TM using $Pd(PPh_3)_4$ as the metal source, we observed an unexpected formation of silylene(SiII)-silyl(Si^{IV})-pincer Pd(II) complex (Scheme 1).⁸ This occurred through a hydride migration from the Pd(II)-H transient species to one of the silylene arms of the ligand. Therefore, we explored alternative routes to [ECE]MX complexes avoiding the

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intermediacy of M-H bonds. Parallel, we sought to expand the coordination chemistry of these ligands to a non precious metal center (e.g. nickel) and explore their potential to increase the electron density on the metal for catalytic applications.

A common way to synthesize complexes bearing a $C(sp^2)$ -M^{II}-X motif is the oxidative addition of a suitable M^o precursor into a $C(sp^2)$ -X bond. Consequently we envisioned preparing the nickel complexes of ECE pincer ligands from the reaction of ECBrE (E = Si, Ge) compounds with Ni(cod)₂ (cod = 1,5-cyclooctadiene) as a Ni^o source. However, the synthesis of the ECBrE starting material was challenging, and just successful results were obtained for the **GeCBrGe** ligand. Slow addition of two molar equiv of LHMDS in toluene to a mixture of 2-bromo-4,6-di-*tert*-butylresorcinol and two molar equiv of the *N*,*N*²-di-*tert*-butylchloro(phenylamidinate)germanium(II) at room temperature produced a new species. The ¹H NMR spectrum of this compound contained two singlets for the *tert*-butyl groups with the relative ratio of 1:2. Purification by extraction with *n*-hexane and recrystallization produced the desired ligand **GeCBrGe** in 68% yield as a colorless solid (Figure 2). **GeCBrGe** was fully characterized by ¹H and ¹³C NMR, mass spectrometry and single-crystal X-ray diffraction analysis (See experimental section and supporting information, *SI*). Its structural features are similar to those of the GeCHGe ligand.⁷ Reversing the addition sequence of the reactants led to the formation of an insoluble purple product of unknown composition. Unfortunately, attempts to obtain the silicon analogue **SiCBrSi** from the bromoresorcinol repeatedly led to undefined products.



Figure 2. Synthesis and molecular structure of the novel **GeCBrGe** pincer ligand. Selected distances [Å] and angles [°] C1-Br1 1.905(3), O1-Ge1 1.862(2), O2-Ge2 1.868(2), C2-O1 1.347(3), C6-O2 1.355(3), Ge1-N1 2.031(3), Ge2-N4 2.021(2), C2-O1-Ge1 142.6(2), C6-O2-Ge2 136.3(2), N1-Ge1-N2 64.8(1), N3-Ge2-N4 64.8(1). Thermal ellipsoids are drawn at a 50% probability level; hydrogen atoms are omitted for clarity. *See Supporting Information* for details.

Synthesis of [ECE]NiBr complexes. The reaction of **GeCBrGe** with Ni(cod)₂ in toluene solution at -30°C furnished a new species, as determined by ¹H NMR spectroscopy. The C_{2v} symmetry determined by the two singlets for the *tert*-butyl groups with the relative integral ratio of 1:2 and its mass spectrum (M⁺: exp. 966.20721 ; cald. 966.20510) showed unambiguously the formation of the desired **[GeCGe]NiBr** pincer complex. This complex was isolated by extraction and recrystallization from *n*-hexane as a red powder in 88% yield (Scheme 2).

Because the silicon analogue could not be prepared by this route, we explored the possibility of synthesizing the pincertype **[ECE]NiBr** complexes via reaction of the ECHE ligands (E = Si, Ge) with NiBr₂(dme) (dme = 1,2-dimethoxyethane). This reaction conducted with the **SiCHSi** ligand precursor in the presence of 10 molar equivalents of NEt₃ in a refluxing THF/toluene solvent mixture led to change in color from dark blue to yellow within 4 hours and with **GeCHGe** under the same conditions to a change in color from dark blue to dark red. The ¹H NMR spectroscopic investigation of the isolated Ni complexes showed the same features for the **[GeCGe]NiBr** complex obtained by oxidative addition of the C(*sp*²)-Br bond

described above. The absence of the phenyl C-H ¹H NMR resonance corresponding to the proton between the silylene donor arms and the sole resonance at δ = 20.2 ppm in the ²⁹Si{¹H} NMR spectrum of [SiCSi]NiBr are consistent with the formation of the desired pincer complex having a square-planar coordinated Ni(II) (Scheme 2). Single crystals suitable for additional characterization and structural elucidation by X-ray diffraction analysis were obtained for both complexes at ambient temperature in concentrated *n*-hexane solutions or by layering toluene solutions of **[SiCSi]NiBr** and **[GeCGe]NiBr** with *n*-hexane, respectively (Figure 3).¹² Their molecular structures bearing square-planar Ni(II) sites were confirmed by X-ray diffraction analyses.

Scheme 2. Synthesis of the [ECE]NiBr pincer-like complexes (E = Si, Ge).



For direct comparison with the well known phosphane pincer ligands, we prepared the analogous nickel complex containing the sterically and isoelectronically related P^{III}- pincer analogue PCHP.⁷ Following the nickel metallation procedure for the ligands **ECHE** using NiBr₂(dme) (Scheme 2), the **[PCP]NiBr** complex was obtained in 95% yield (Figure 3c). Its ¹H NMR spectrum is consistent with a C_{2v} symmetric structure. This spectrum contained one doublet and one septet for the isopropyl group, and a single singlet resonance for the *tert*-butyl groups in the relative ratio of 12:2:9, as well as a singlet in the ³¹P NMR spectrum at 134.6 ppm. This structural assignment was confirmed by X-ray diffraction analysis. As observed for the **[ECE]NiBr** complexes (E = Si, Ge), the Ni(II) sites have a square planar geometry (Figure 3c). Comparing the bond distances in the crystal structures depicted in Figure 3, the E-Ni distances vary in accordance with the covalent radii of the donor atom. However, there is a slight difference in the Ni-Br distances depending on the donor atom E at the pincer arms **[ECE]**. The Ni-Br and C_{ipso}-Ni distances increased accordingly to the σ -donor strength of the ligand. This is in accordance with the order established previously for the same ligand series on the iridium(III) olefinic complexes [ECE]IrHCl(coe) (E = P < Ge ≤ Si). The C-Ni bond is longer in about 5-8 pm for the complexes with Si and Ge as donors comparing with the P^{III}-isoelectronic complex, respectively. Moreover, this effect is slightly lower for the Ni-Br bond distance where an increment of 1 pm is observable for the **[SiCSi]NiBr** complex.



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Figure 3. Molecular structures with selected distances [Å] and angles [°] of a) **[SiCSi]NiBr**: C1-Ni1 1.927(2), Br1-Ni1 2.3410(5), Si1-Ni1 2.1737(7), Si2-Ni1 2.1716(7), C1-Ni1-Br1 178.51(7), Si1-Ni1-Si2 161.75(3), C6-O1-Si1 110.8(1), C2-O2-Si2 110.5(1), Σ<Ni1 360.02(7); b) **[GeCGe]NiBr**: C1-Ni1 1.961(3), Br1-Ni1 2.3351(5), Ge1-Ni1 2.2113(6), Ge2-Ni1 2.2190(6), C1-Ni1-Br1 178.5(1), Ge1-Ni1-Ge2 165.42(2), C2-O1-Ge1 109.9(2), C6-O2-Ge2 110.7(2), Σ<Ni1 360.0(1); c) **[PCP]NiBr**: C1-Ni1 1.881(4), Br1-Ni1 2.3297(7), P1-Ni1 2.136(2), P2-Ni1 2.151(2), C1-Ni1-Br1 178.0(2), P1-Ni1-P2 165.36(5), C2-O1-P1 111.6(3), C6-O2-P2 113.5(3), Σ<Ni1 360.1(1). Thermal ellipsoids are drawn at a 50% probability level; hydrogen and solvent atoms are omitted for clarity. *See Supporting Information* for details.

Nickel-Catalyzed Sonogashira Cross Coupling. We initially assessed the reactivity of the **[ECE]NiBr** pincer complexes as catalyst for the Sonogashira reaction of (*E*)-1-iodo-1-octene with phenylacetylene as test substrates (Scheme 3). The reaction conducted with 5 mol % of E = Si, Ge and an excess of the halide substrate occurred in moderate yields. These yields are comparable to those of the isoelectronic P^{III}-based reference system **[PCP]NiBr**. The catalytic reaction mixtures with the **[ECE]NiBr** (E = Si, Ge, P) complexes turned dark to black, indicating the formation of Ni^o. This observation raised the question of whether the metallylene systems are stable under the reaction conditions and if the typical elementary steps of oxidative addition, transmetallation, and reductive elimination account for the catalytic activity. To the best of our knowledge, a defined chemical transformation at a metal center decorated with metallylene scaffolds has not been reported in the literature yet. This is of general interest since metallylenes are prone to undergo chemical reactions with great variety of functional groups.^{5,6} Therefore we explored stoichiometric reactions to identify possible intermediates of the Sonogashira reaction, including i) transmetallation on the Ni(II) center with the copper acetylide, ii) oxidative addition of the alkenyl iodide and iii) reductive elimination to produce the coupling product and regenerate the Ni(II) active species.

Scheme 3. Evaluation of the **[ECE]NiBr** (E = Si, Ge, P) complexes as pre-catalysts in the Sonogashira cross coupling reaction.



Stepwise Stoichiometric Reaction with Copper Acetylides. To investigate the first elementary step of the mechanism (i.e. transmetallation), copper phenylacetylide, as well as the 4-methoxy and 3,5-bis-trifluoromethyl substituted derivatives were synthesized following the reported procedures.¹³ The Cu-acetylides are not soluble in either benzene or toluene, but two molar equiv reacted as a slurry with **[SiCSi]NiBr** in C₆D₆ over 3-4 hours. NMR spectroscopic characterization of the reaction mixture after filtration through Celite showed that a new product with C_{2v} symmetry was formed. This symmetry was shown by one *tert*-butyl resonance in the ¹H NMR spectrum and one singlet resonance in the ²⁹Si{¹H} NMR spectrum (Scheme 4).

Scheme 4. i) Investigation of possible elementary steps through stoichiometric transformations. ii) Sequential ¹H and ²⁹Si NMR spectra for the course of the coupling reaction.



The products of this transmetallation were only moderately stable in solution for a couple of hours and gave a black precipitate upon evaporation of the solvent. The original signals for **[SiCSi]NiBr** reappeared partially in the ¹H NMR spectra and the homocoupled phenylacetylenes (C=C-Ph-R)² were observed in the GC-MS. These data indicate, that i) not all of the CuBr formed in the transmetallation could be removed by simple filtration, and ii) that the intermediate Ni-acetylides – if formed – reacted in a bimolecular reaction to form the bis-acetylenes, Ni^o and undefined organic products from the ligand.

To probe for a bimolecular decomposition pathway, the solutions generated by reaction of **[SiCSi]NiBr** with [Cu-C=C-Ph]_n and [Cu-C=C-3,5-(CF₃)₂Ph]_n were combined. The reaction products were analyzed by GC-MS after one day at room temperature. The mixed diyne Ph-C=C-C=C-3,5-(CF₃)₂Ph was detected. Further characterization of the crude Ni-acetylides in solution by Atmospheric Pressure Chemical Ionization – Mass Spectrometry (APCI-MS) showed three molecular ions in each case: **[SiCSi]NiBr** as the most intense signal, one signal for the expected Ni-acetylides [SiC-Si]Ni-C=C-Ph-R and one signal for an adduct {[SiCSi]Ni-C=C-Ph-R→CuBr} (Figure 4a). The signals for the latter two species were approximately equal in intensity.

Single crystals were obtained from the reaction of **[SiCSi]NiBr** with (Cu-CC-Ph)_n after microfiltration of the reaction mixture and storage in a mixture of *n*-pentane and toluene as solvent at -78 °C over approximately one week. Interestingly, the structure determined by X-ray diffraction corresponded to the **{[SiCSi]Ni-C=C-Ph→CuBr}** adduct (Figure 5a). This structure consists of a copper center in close proximity to the C=C bond and the silylene unit (vide infra for a detailed discussion). Moreover, after re-dissolving the crystals in C₆D₆, the same mass spectrum with the three species and the symmetric NMR data as described above were obtained.



Figure 4. APCI-MS and calculated spectra for the transmetallation intermediates a) **{[SiCSi]Ni-CC-Ph→CuBr}** and b) **{[SiCSi]Ni-CC-terPh→CuBr}**

Transmetallation reactions between the synthesized Cu-phenylacetylides and **[GeCGe]NiBr** occurred in a fashion similar to the reactions with **[SiCSi]NiBr**, but full conversion to the Ni-phenylacetylides intermediates were not observed. However, the products were less stable and decomposed in the presence of larger quantities of the Cu-phenylacetylides. The dependence of the stability of the transmetallation products on the amount of Cu-phenylacetylide implies that at least one of the decomposition pathways of the Ni-phenylacetylide complexes is bimolecular. Thus, we sought to sterically block the Ni center by conducting analogous reactions with a *meta*-terphenylacetylide compound (Scheme 5).

Scheme 5. Synthesis of kinetic stabilized [ECE]Ni-C=C-terPh→CuBr intermediates.



Copper-terphenylacetylide reacted cleanly with each of the metallylene pincer **[ECE]NiBr** (E = Si, Ge) complexes. As anticipated, the products were stable in solutions for several days without noticeable decomposition. The ¹H NMR spectrum of the bis-germylene derivative showed the same C_{2v} symmetry as described for the intermediates above, but the signals for the *tert*-butyl groups on the amidinate arms in the bis-silylene complex were as broad singlets. This line shape could be due to i) steric interactions between the silylene subunits and the terphenyl group, or ii) the reversible formation of an adduct with CuBr, thereby breaking the C_{2v} symmetry. The APCI-MS of the crude reaction contained three sets of signals for the **[ECE]NiBr** precursors, the [ECE]Ni-C=C-*ter*Ph transmetallation product, and the CuBr

adduct of the transmetallation product (the signal due to the adduct was more intense than it was for the non-sterically hindered acetylides; Figure 4b). This kinetic stabilization of the transmetallation product by steric hindrance allowed us to crystallize the copper acetylene adduct bound by the bis-germylene ligand at room temperature without any no-ticeable decomposition. The structure determined by X-ray diffraction data again revealed the formation of the adduct $\{[GeCGe]Ni-C=C-terPh \rightarrow CuBr\}$ (Figure 5b).

Transmetallation experiments with the phosphane analogue **[PCP]NiBr** with [Cu-C=C-Ph]_n and [Cu-C=C-*ter*Ph]_n showed similar reactivity to the **[ECE]NiBr** complexes. However, the equilibrium is strongly shifted to the starting Ni-Br complex (see SI for NMR and MS data) and no desired product could be isolated. Reaction with 5 molar equiv of $[Cu-C=C-Ph]_n$ at 60°C for 12 h furnished the transmetallation product in 5% conversion determined by ³¹P NMR spectroscopy. Analysis by APCI-MS showed two molecular ion peaks for the [PCP]NiBr and [PCP]NiCCPh complexes, the latter with lower intensity. No CuBr adduct could be observed in this case. The difference in reactivity can be explained by the higher electron density at the Ni center in the [ECE]NiBr complexes which enables a stronger π -backbonding interaction with the C=C bond, leading to a higher stability of the transmetallation product.¹⁴



Figure 5. Molecular structures with selected bond lengths [Å] and angles [°] of a) **{[SiCSi]Ni-C=C-Ph→CuBr}**: Ni1-Si1 2.296(1), Ni1-Si2 2.137(1), Ni1-C9 1.940(4), Ni1-C1 1.860(4), Ni1-Cu1 2.4628(9), Si1-Cu1 2.508(1),C1-Cu1 1.976(4), C2-Cu1 2.420(4), C1-C2 1.213(6), C2-C3 1.451(6), Cu1-Br1 2.2855(7), Si1-Ni1-Si2 160.93(5), C1-Ni1-C9 162.9(2), Ni1-Si1-Cu1 61.49(3), C10-O1-Si1 115.4(2), C14-O2-Si2 110.4(2), Σ <Ni1 360.1(1); b) **{[GeCGe]Ni-C=C-terPh→CuBr}**: Ni1-Ge1 2.3254(6), Ni1-Ge2 2.1786(6), Ni1-C9 1.985(3),Ni1-C1 1.890(4), Ni1-Cu1 2.5208(7), Ge1-Cu1 2.5450(6),C1-Cu1 1.951(3), C2-Cu1 2.403(3), C1-C2 1.216(5), C2-C3 1.437(5), Cu1-Br1 2.2855(7), Ge1-Ni1-Ge2 161.09(3), C1-Ni1-C9 164.1(2), Ni1-Ge1-Cu1 62.15(2), C10-O1-Ge1

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113.4(2), C14-O2-Ge2 109.0(2), Σ <Ni1 360.4(1). Thermal ellipsoids are drawn at a 50% probability level; hydrogen and solvent atoms are omitted for clarity. See *Supporting Information* for details.

Isolated Intermediates, Their Structural Features and DFT Calculations. The coordination of the copper to the acetylide unit renders the structures in Figure 5 unsymmetrical. The **E-Ni** (E = Si, Ge) distances between the CuBr-coordinated side (d(Ni-Si1) = 2.296 Å, d(Ni-Ge1) = 2.325 Å) and the non-coordinated side (d(Ni-Si2) = 2.137Å, d(Ni-Ge2) = 2.179 Å) are different in both **{[ECE]Ni-C=C-Ph/terPh→CuBr}** complexes. In addition, the copper atom is much closer to the C1 atom (d(Cu-C1) = 1.976 Å, 1.944 Å for E = Si, Ge, respectively) of the acetylide ligand than to the remote C2 atom (d(Cu-C2) = 2.420 Å, 2.441 Å for E = Si, Ge, respectively). The unsymmetrical binding of the copper is different from a "classical-side-on" coordination in which Δd (Cu-C1 vs. Cu-C2) is less than 0.150 Å.¹⁵ Additionally, the <(C1=C2-C3) and <(Ni-C1=C2) angles are indicative of a C=C→Cu bond (side-on: ca. 156-165°; end-on: ca. 170°-180° ^{15f.g}) and show, if at all, only minor perturbation of the C=C bond (Si: 170.5° and 174.9°; Ge: 171.5° and 176.4°). The arms of the pincer ligands open towards the Cu atom in accordance with a reduction of the <(O1-E1-N) angles (average change: Si: 106.75°→99.45°; Ge: 106.41°→97.12°) and shortening of the Cu-E distances (d(Cu-Si) = 2.5080 Å; d(Cu-Ge) = 2.5704 Å), indicating a E→Cu bond.

To understand the bonding in the four member ring (C1-Ni-Si1-Cu), we conducted detailed density functional theory (DFT) calculations for both **{[ECE]Ni-C=C-Ph/terPh**→**CuBr}** intermediates (E = Si, Ge) with B3LYP-D3(BJ)/def2-TZVP¹⁶⁻¹⁸ functionals. For comparison, the corresponding **[ECE]Ni-C=C-Ph/terPh** complexes lacking bound CuBr were also computed (see experimental section for computational details). Computations were conducted on i) fully op-timized structures (fullopt) and ii) the X-ray crystal structures after reoptimization of the hydrogen-atom positions (crystal/H-opt). We focused mostly on atomic charges from natural population analysis (NPA) and on a real space description by the electron localization function (ELF)¹⁹ or the related electron localizability indicator (ELI-D).²⁰ The bond distances of the fullopt structure agree well with those of the crystal/H-opt structure (Table 1). The main effect of CuBr coordination in all cases is lengthening of the **E1-Ni** bond and concomitant shortening of the **E2-Ni** bond opposite to the CuBr fragment. Interestingly, the bending of the phenylacetylide ligand out of a straight C_{ipso}-Ni-C-C arrangement in both complexes with CuBr is accompanied by a slight but significant lengthening of the alkyne triple bond and of the C2-C3 single bond.

		bond length [Å]							
	{[EC	{[ECE]Ni-CC-R→CuBr}				{[ECE]Ni-CC-R}			
Bond	crystal/H-opt ^b		fullopt-D3 ^b		fullopt-D3 ^b				
	E=Si	E=Ge	E=Si	E=Ge	E=Si	E=Ge			
E1-Ni	2.296	2.317	2.319	2.329	2.181	2.199			
E2-Ni	2.137	2.181	2.131	2.178	2.182	2.196			
Ni-C1	1.861	1.881	1.866	1.885	1.848	1.858			
C1-C2	1.212	1.219	1.233	1.232	1.222	1.224			
C2-C3 (ipso,R ^c)	1.452	1.444	1.420	1.423	1.413	1.414			
Cu-C1	1.976	1.948	2.020	1.998					

Table 1. Selected bond lengths in complexes {[ECE]Ni-CC-R \rightarrow CuBr} and {[ECE]Ni-CC-R} (E=Si, R=Ph / E=Ge, R=terPh)^a

Cu-C2	2.420	2.422	2.528	2.551	
Cu-E1	2.508	2.558	2.496	2.548	
Cu-Ni	2.462	2.526	2.485	2.531	
Cu-Br	2.286	2.285	2.318	2.306	

^a For atom number assignment see Figure 5.

^b B3LYP/def2-TZVP results (cf. Computational details). ^c C ipso of the phenylacetylide ligand.

The ELF plot displayed in Figure 6 shows that the Cu atom is involved in a three-center bond with **E1** and **Ni** (ELI-D gives a qualitatively similar bonding description, Table S6 in *SI*). While no interaction of Cu with the acetylide ligand is apparent in the ELF, an appreciable **Cu-C1** Mayer bond order (Si: 0.963; Ge: 0.855) suggests that there are bonding interactions between Cu and the acetylide ligand (See Table S4 for further values). The reduced C=C bond order in the full optimized structures containing the bound CuBr (Si: 0.728, Ge: 1.321), as compared to the C=C bond order in the system lacking CuBr (Si: 1.737; Ge: 2.076) is in agreement with a bonding interaction between C1 and the Cu center. NPA charges (Tables S2 and S3) show that CuBr receives about 0.2 electrons form the complex, and **E1** becomes more negative by about 0.18 electrons for E = Si and by about 0.13 electrons for E = Ge. Closer examination shows that this charge results mainly from **Ni** and the **E2** atom on the opposite side, with smaller contributions from other parts of the ligand framework. This charge distribution is consistent with a charge transfer towards the newly formed **E1-Cu-Ni** three-center bond (Figures 5 and 6). Overall, a pattern of delocalized interactions emerges that allows the CuBr fragment to bond to the combination of Ni, one metallylene arm from the pincer moiety, and the acetylide coligand.



{[GeCGe]Ni-CC-terPh→CuBr}

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Figure 6. ELF plot in the main Ni coordination plane for **{[ECE]Ni-CC-Ph/terPh→CuBr}** (E= Si, Ge) (B3LYP-D3/def2-TZVP level).

After the complete analysis by the spectroscopic methods and DFT calculations of the **{[ECE]Ni-CC-Ph/terPh** \rightarrow **CuBr}** complexes, we conclude that the first step of the catalytic reaction occurs via a transmetallation process forming the CuBr adduct in solution with a medium half-life time. Consequently, to study the next elementary step the transmetallation products were generated *in situ* and used after microfiltration.

Stepwise Stoichiometric Reaction with (*E***)-1-Iodo-1-octene.** One a possible scenario for the observed Sonogashira coupling is the sequence of transmetallation, oxidative addition, and reductive elimination. In this sequence, oxidative addition of the substrate containing a C(*sp*²)-halide bond would occur to the nickel-acetylide. Indeed, addition of three molar equiv of (*E*)-1-iodo-1-octene to solutions of the *in situ* generated {[SiCSi]Ni-phenylacetylides→CuBr} in C₆D₆ formed the C-C coupled products in yields from 80-95% (determined by GC/MS) after a few hours at 50 °C in combination with **[SiCSi]NiI** (Scheme 4). The spectroscopic features for the latter species were confirmed by the independent synthesis of the nickel iodide complex. This complex was prepared by the same procedure applied for the bromide analogue but using NiI₂(dme) as the metal precursor instead, and fully characterized by ¹H and ²⁹Si NMR spectroscopies, APCI-MS and X-ray analysis (see experimental section and *SI* for further details). The formation of the coupled product and the nickel iodide is consistent with a combination of oxidative addition and reductive elimination. The X-ray structure of **[SiCSi]NiI** resembles the structural features of **[SiCSi]NiBr** concluding that no alteration on the ligand backbone has occurred after closing the catalytic cycle. At this stage, there is no evidence of the reaction intermediate for this elementary step. However, the perseverance of the *E* stereochemistry on the final product evidenced by ¹H NMR spectroscopy suggested the oxidative addition and subsequent reductive elimination as the most likely pathway.

Reaction Mechanism. The investigation of stoichiometric transformations reveals a general mechanism for the C-C coupling between phenylacetylene and (*E*)-1-iodo-1-octene catalyzed by **[ECE]NiBr** complexes (Scheme 6). The [ECE]NiX (E = Si or Ge, X = Br or I) complex reacts with the Cu-phenylacetylide generated *in situ* between the phenylacetylene and the CuI in the presence of Cs_2CO_3 . The product of this transmetallation process binds CuBr to form the {[ECE]Ni-C=C-Ph→CuBr} species. This species reacts with the alkenyl halide to form the organic product and regenerate the nickel halide. One possible sequence to form these products is oxidative addition and reductive elimination to form **[ECE]NiI** and (*E*)-dec-3-en-1-ynyl-benzene.

Scheme 6. Proposed catalytic cycle



CONCLUSIONS

In summary, the first silvlene and germylene nickel-pincer complexes **[ECE]NiBr** (E = Si, Ge) were synthesised by either a sequence of C-H activation and HBr elimination between **ECHE** and NiBr₂(dme) or C-Br oxidative addition of **GeCBrGe** by Ni(cod)₂. These novel structurally characterized complexes catalyze the Sonogashira coupling between phenylacetylene and (*E*)-1-iodo-1-octene to form (*E*)-dec-3-en-1-ynyl-benzene. Most important, investigation of the proposed mechanism of this unusual nickel-catalyzed Sonogashira reaction by stoichiometric transformations allowed the isolation and structural characterization of a copper-bound nickel acetylide as the sole transmetallation product. This Ni(II) species reacts with alkenyl iodides ($C(sp^2)$ -I) to form a Ni(II) iodide and the coupled product. These results suggest that the electron-rich nickel-pincer complexes with neutral Ge and Si donor atoms can react by a mechanism in which transmetallation precedes reaction with the haloarene. Moreover, the stoichiometric reaction raises the question of the oxidation state of the nickel intermediate that results from C-I bond cleavage and forms the C-C bond of the organic product. Further studies to elucidate the identity of such an intermediate are ongoing.

EXPERIMENTAL SECTION

General Considerations. All experiments and manipulations were conducted under dry oxygen-free nitrogen using standard Schlenk techniques or in a MBraun drybox with an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior use. 1H, 13C, 31P and 29Si NMR spectra were recorded on Bruker AV 400 (1H: 400.13 MHz, ¹³C: 100.61 MHz; ²⁹Si: 79.49 MHz) or AFM 200 (¹H: 200.13 MHz, ¹³C: 50.32 MHz, ¹⁹F: 188.33 MHz, ³¹P: 81.01 MHz) spectrometers. The NMR signals are reported relative to the residual solvent peaks (¹H: CDCl₃: 7.26 ppm; C₆D₆: 7.15 ppm; ¹³C: CDCl₃: 77.0 ppm; C₆D₆: 128.0 ppm), or an external standard (³¹P: 85% H₃PO₄ 0.0 ppm; ²⁹Si: TMS: 0.0 ppm). Single-Crystal Xray Structure Determinations: Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N₂ flow. The data was collected either on an Agilent Technologies X calibur S Sapphire at 150 K (Mo-K α radiation, $\lambda = 0.71073$ Å) or an Agilent Technologies SuperNova (single source) at 150K (Cu-K α radiation, $\lambda = 1.5418$ Å). The structures were solved by direct methods and refined on F2 with the SHELX-97 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Mass spectra were recorded on a Finnigan MAT95S. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR. GC-MS measurements were conducted on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer. NiBr2, NiI2, were purchased from Aldrich. NiBr₂(dme),²¹ NiI₂(dme),²¹ 2-bromo-4,6-di-tert-butylresorcinol,22 N.N'-di-tertbutylchloro(phenylamidinate)germanium(II)²³ were prepared according to the reported procedures, as well as the SiCHSi¹¹ and GeCHGe¹⁰ and PCHP¹⁰ ligands.

Synthesis of GeCBrGe. A solution of 2-bromo-4,6-di-*tert*-butylresorcinol (0.69 g, 2.3 mmol) in 20 mL of toluene was slowly added to a solution *N*,*N*²-di-*tert*-butylchloro(phenylamidinate)germanium(II) (1.54 g, 4.5 mmol) in 20 mL of toluene at room temperature forming a strong yellow reaction mixture. After stirring for 30 min, a solution of LHMDS (0.77 g, 4.6 mmol) in 10 mL of toluene was added dropwise in a period of 30 min with concomitant formation of turbidity and color change to terracotta. All volatiles were removed *in vacuo* after stirring overnight at room temperature and the product was extracted with hot hexane (1x60 mL, 2x20 mL) via cannula filtration. The product was concentrated up to 10 mL and crystallized overnight at -3°C as white crystals. Further filtration and dry *in vacuo* produced 1.40 g of the desired product (68% yield). ¹**H NMR** (400.13 MHz, C₆D₆, 298K): δ (ppm) = 1.07 (s, 36 H, NC(CH₃)₃), 1.83 (s, 18 H, ArC(CH₃)₃), 6.90-7.04 (m, 8 H, arom. H), 7.29-7.32 (m, 2 H, arom. H), 7.61 (s, 1 H, Ar-H). ¹³C{¹H} **NMR** (100.61 MHz, C₆D₆, 298K): δ (ppm) = 31.5 (ArC(<u>C</u>H₃)₃), 32.2 (NC(<u>C</u>H₃)₃), 35.8 (Ar<u>C</u>(CH₃)₃), 53.1 (N<u>C</u>(CH₃)₃), 111.6 (C_{arom}Br), 123.4 (C_{arom}H), 129.6 (C_{arom}tBu), 127.4, 129.2, 129.9, 136.0 (C_{arom}H), 156.9 (C_{arom}O), 170.3 (NCN). **APCI-MS** (m/z): calcd for [C₄₄H₆₅BrGe2N₄O₂^{•+}] 908.26975; found 908.26978 (correct isotope pattern). **Elemental analysis** for C₄₄H₆₅BrGe₂N₄O₂: calc: C 58.25, H 7.22, N 6.18; found: C 58.45, H 7.35, N 6.18.

Synthesis of [ECE]NiX (E = Si, Ge, P; X = Br, I) complexes. General procedure with NiBr₂(dme): NEt₃ (10.0 equiv.) were added to a suspension of NiBr₂(dme) (1.1 equiv.) in THF forming a dark blue solution. After stirring for 20 min, a solution of **ECHE** (1.0 equiv.) in toluene was added via cannula and the reaction mixture was heated to reflux for 4 h. The mixture was allowed to cool to room temperature, filtered through a short plug of Celite and all volatiles were removed *in vacuo*. The residue was extracted with hexane (1x50 mL, 2x20 mL) at 50°C. The combined organic solutions were concentrated slowly *in vacuo* until small crystals formed at the glass wall. Further cooling in the freezer at -30°C resulted in the crystallization of the pure products in form of needles, which were collected by filtration and dried *in vacuo* for 2 h.

[SiCSi]NiBr (1.4 mmol scale: 70% yield; yellow needles): ¹H NMR (400.13 MHz, C₆D₆, 298K): δ (ppm) = 1.34 (s, 36 H, NC(CH₃)₃), 1.75 (s, 18 H, ArC(CH₃)₃), 6.79-6.91 (m, 8 H, CH_{arom}), 7.48 (s, 1 H, CH_{arom}), 7.69-7.71 (m, 2 H, CH_{arom}). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298K): δ (ppm) = 30.8 (s, ArC(CH₃)₃), 31.5 (s, NC(CH₃)₃), 35.3 (s, ArC(CH₃)₃), 54.1 (s, NC(CH₃)₃), 123.8 (s, CH_{arom}), 126.5 (s, C_{arom}tBu), 128.4 (s, CH_{arom}), 130.3 (s, 2C, CH_{arom}), 131.3 (s, CNi), 131.4 (s, C_{arom}), 162.7 (s, C_{arom}O), 173.1 (s, NCN). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 298K): δ (ppm) = 20.22. APCI-MS (m/z): calcd for [C₄₄H₆₅BrN₄NiO₂Si₂⁻⁺] 874.31774; found 874.31805 (correct isotope pattern). Elemental analysis for C₄₄H₆₅BrN₄NiO₂Si₂.C₆H₁₄: calcd: C 62.36, H 8.27, N 5.82; found: C 62.72, H 8.43, N 6.22.

[SiCSi]NiI. NiI₂(dme) as the precursor (0.3 mmol scale: 66% yield; orange needles): ¹H NMR (200 MHz, C₆D₆, 298K): δ (ppm) = 1.33 (s, 36 H, NC(CH₃)₃), 1.77 (s, 18 H, ArC(CH₃)₃), 6.80-6.97 (m, 8 H, CH_{arom}), 7.54 (s, 1 H, CH_{arom}), 7.85-7.88 (m, 2 H, CH_{arom}). ¹³C{¹H} NMR (50.32 MHz, C₆D₆, 298K): δ (ppm) = 30.8 (s, ArC(CH₃)₃), 31.5 (s, NC(CH₃)₃), 35.4 (s, ArC(CH₃)₃), 54.1 (s, NC(CH₃)₃), 123.9 (s, CH_{arom}), 126.6 (s, Carom*t*Bu), 130.2 (s, CH_{arom}), 130.3 (s, CH_{arom}), 131.4 (s, Carom), 135.7 (s, CNi), 162.5 (s, CaromO), 173.4 (s, NCN). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, 298K): δ (ppm) = 30.70. APCI-MS (m/z): calcd for [C₄₄H₆₅IN₄NiO₂Si₂^{•+}] 922.30387; found 922.30396 (correct isotope pattern). Elemental analysis for C₄₄H₆₅IN₄NiO₂Si₂: calc.: C 57.21, H 7.09, N 6.06; found: C 56.44, H 6.47, N 7.17.

[GeCGe]NiBr (0.5 mmol scale, 57% yield; red needles): ¹H NMR (400.13 MHz, C₆D₆, 298K): δ (ppm) = 1.21 (s, 36 H, NC(CH₃)₃), 1.83 (s, 18 H, ArC(CH₃)₃), 6.78-6.91 (m, 8 H, CH_{arom}), 7.06-7.10 (m, 2 H, CH_{arom}), 7.56 (s, 1 H, CH_{arom}). ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298K): δ (ppm) = 31.0 (s, ArC(CH₃)₃), 31.5 (s, NC(CH₃)₃), 35.8 (s, ArC(CH₃)₃), 54.4 (s, NC(CH₃)₃), 125.1 (s, CH_{arom}), 125.4 (s, CaromCtBu), 126.8 (s, Carom), 128.7 (s, CH_{arom}), 128.7 (s, CH_{arom}), 130.0 (s, CH_{arom}), 132.3 (s, CNi), 162.6 (s, CaromO), 175.0 (s, NCN). APCI-MS (m/z): calcd for [C₄₄H₆₅BrGe₂N₄NiO₂^{•+}] 966.20510; found 966.20721 (correct isotope pattern). Elemental analysis for C₄₄H₆₅BrGe₂N₄O₂: calc. C 54.71, H 6.78, N 5.80; found: C 54.22, H 7.06, N 5.51.

[PCP]NiBr (95% yield, yellow needles). ¹H NMR (200.13 MHz, CDCl₃, 298K): δ (ppm) = 1.31 (s, 18H, C(CH₃)₃), 1.32 (d, ³J_{HH} = 6.6 Hz, 24 H, CH(CH₃)₂), 3.25 - 3.32 (m, 4H, CH2), 3.33 - 3.39 (m, 4H, CH₂), 3.73 - 3.86 (m, 4H, CH(CH₃)₂), 6.93 (br. s, 1H, CH_{arom}). ¹³C{¹H} NMR (50.32 MHz, CDCl₃, 298K): δ (ppm) = 21.8 (t, ²J_{CP} = 2.5 Hz, PC(<u>C</u>H₃)₃), 22.6 (t, ²J_{CP} = 2.8 Hz, PC(<u>C</u>H₃)₃), 29.9 (s, ArC(<u>C</u>H₃)₃), 43.5 (s, CH₂), 47.1 (t, ²J_{CP} = 7.1 Hz, P<u>C</u>(CH₃)₃), 123.8 (s, CH_{arom}), 126.2 (t, ³J_{CP} = 5.7 Hz, Carom), 134.2 (t, ¹J_{CP} = 24.7 Hz, CNi), 156.5 (t, ²J_{CP} = 13.2 Hz, CO). ³¹P{¹H} NMR (81.01 MHz, CDCl₃, 298K): δ (ppm) = 134.6 (s). HR-EI-MS (m/z): calcd for [C₃₀H₅₅BrN₄NiO₂P₂^{•+}] 704.23166; found 704.17770 (correct isotope pattern).

Procedure with GeCBrGe and Ni(cod)₂: Ni(cod)₂ (0.15 g, 0.53 mmol) was dissolved in 20 mL of toluene at -30°C. A solution of **GeCBrGe** (0.53 g, 0.58 mmol) in 20 mL of toluene was added dropwise through a syringe. The stirred reaction mixture was slowly warmed up to room temperature over the course of 8 h, resulting in a dark red solution, which was filtered. All volatiles from the filtrate were removed *in vacuo*, and the solid was washed with cold hexane (2x10 mL). The residue was dried *in vacuo* for 2 h, obtaining **[GeCGe]NiBr** as a dark red powder (0.45 g, 88 % yield).

Catalytic Sonogashira Cross Coupling. In a nitrogen filled drybox, [ECE]NiBr (5 mol-%; 11.4 µmol), CuI (1.1 mg, 5 mol-%; 11.4 µmol), Cs₂CO₃ (74.0 mg, 228.0 µmol), phenylacetylene (11.6 mg, 114 µmol) and (*E*)-1-iodooct-1-ene (1-5 eq) were

weighted in a 4.0 mL screw cap vial containing a stir bar, and dissolved in 1.5 mL 1,4-dioxane. The sealed vial was removed from the drybox and heated to 100°C for 24h in a temperature controlled heating block. After cooling, the mixture was filtered through short plug of silica and all volatile materials were evaporated *in vacuo*. The yields of the products were determined by redissolving the crude product in CDCl₃ and adding a defined amount of CH₂Br₂ as internal reference; and/or by addition of a defined amount of dodecane as internal standard to the reaction mixture before heating and taking small aliquots for analysis by GC-MS.

Stoichiometric Reactions with Copper Acetylides. In a nitrogen filled drybox, [ECE]NiBr (0.02-0.07 mmol), [Cu-CC-Ph-R] (0.03-0.09 mmol) were weighted in a Schlenk flask or in a capped vial containing a stir bar and dissolved in the appropriate solvent (toluene or C₆D₆). The sluggish reaction mixture was stirred for 4h and filtered through a short plug of Celite. Suitable crystals of {[SiCSi]Ni-CC-Ph \rightarrow CuBr} for X-ray analysis were grown at -78°C after several micro filtrations in a solvent mixture *n*-pentane (1:1). For the complex {[GeCGe]Ni-CC-*ter*Ph \rightarrow CuBr} the crystals were grown layering *n*-pentane on the toluene solution at room temperature.

Quantum Chemical Calculations. Computational details. All structures were optimized at the B₃LYP/def2-TZVP level of theory using the Turbomole 6.31 program package.²⁴ That is, the global hybrid functional B₃LYP²⁵ with 20% of the exact Hartree-Fock exchange admixture, in conjunction with standard Turbomole all-electron def2-TZVP basis sets²⁶ for all atoms. For the full optimization Grimme's dispersion correction 3 with the Becke-Johnson potential was used.²⁷ The crystal structures of **{[ECE]Ni-CC-Ph/terPh→CuBr}** complexes were used as initial structures for full optimization (denoted as "fullopt-D3"). For comparison, partial optimization of only the hydrogen-atom positions for the X-ray-based structure of **{[ECE]Ni-CC-Ph/terPh→CuBr}** was also done at the B₃LYP/def2-TZVP level (denoted as "crystal/opt-H"). For full optimization of the **{[ECE]Ni-CC-Ph/terPh→CuBr}** were taken and the CuBr removed.

Atomic charges were evaluated at the B3LYP/def2-TZVP level of theory by means of natural population analyses (NPA), using the built-in NBO subroutines of the Gaussian 09 program.²⁸ Mayer bond orders²⁹ were evaluated using the program BORDER.³⁰ The wavefunctions were also analyzed in the DGrid program³⁰ by means of the electron localization function (ELF)³¹ and the electron localizability indicator based on the parallel-spin electron pair density (ELI-D).³² For this purpose, the Kohn-Sham orbitals of the (Gaussian 09) single point calculations were transferred to the DGrid and the examined property was calculated on a grid with 100 points per Bohr. The results of ELF analyses was visualized using the Paraview program.³³

ASSOCIATED CONTENT

Experimental details about synthesis of organic precursors. NMR, APCI-MS, XRD experimental data and calculated Mayer bond orders, NPA charges and ELF-D, ELI-D plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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ABBREVIATIONS

APCI-MS, Atmospheric Pressure Chemical Ionization-Mass Spectrometry; NPA, Natural Population Analyses; ELF, Electron Localization Function; ELI, Electron Localizability Indicator.

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