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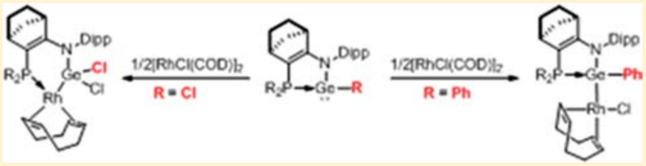
Synthesis and Characterization of Rhodium Complexes with Phosphine-Stabilized Germylenes

Juan M. García,[‡] Edgar Ocando-Mavárez,*[,‡] Tsuyoshi Kato,[†] David Santiago Coll,[§] Alexander Briceño,[∥] Nathalie Saffon-Merceron,[⊥] and Antoine Baceiredo*[,†]

[†]Université de Toulouse, UPS and CNRS, LHFA UMR 5069, F-31062 Toulouse, France
[‡]Laboratorio de Fisico-Química Orgánica, IVIC, Caracas 1020-A, Venezuela
[§]Laboratorio de Fisico-Química Teórica de Materiales, IVIC, Caracas 1020-A, Venezuela
[∥]Laboratorio de Síntesis y Caracterización de Nuevos Materiales, IVIC, Caracas 1020-A, Venezuela
[⊥]Université de Toulouse, UPS and CNRS, ICT FR 2599, F-31062 Toulouse, France

S *Supporting Information*

ABSTRACT: The reaction of phosphine-stabilized germylenes (**1a**,**b**) with dimer complex [$Rh_2(\mu\text{-}Cl)_2(COD)_2$] leads to the corresponding phosphine−germylene−Rh(I) complexes (**2a**,**b**). Interestingly, the stability of these complexes depends strongly on the nature of the substituent of the germylene fragment. Indeed, the complex (**2a**) with the chloro-germylene ligand isomerizes into a metallacycle rhodium complex (**3a**) via germylene insertion into the Rh−Cl bond, while the complex with the phenyl-substituted germylene (**2b**) was isolated and represents the first stable Rh(I)−germylene complex with a Rh−Cl bond.



INTRODUCTION

In past decades, germylene compounds have attracted growing interest not only as synthetic tools in organic chemistry but also for their potential use as ligands for transition metals.[1,2] Usually, germylenes are highly reactive derivatives and tend to oligomerize or polymerize; however, they can be stabilized kinetically by sterically demanding substituents[1] and/or thermodynamically by inter- or intramolecular coordination of Lewis base ligands.[3] Therefore, numerous four-, five-, and six-membered N-heterocyclic germylenes have been isolated by using nitrogen-containing bulky ligands.[3−5] The stabilization strategy using neutral donor ligands led to the formation of three-coordinate Ge(II) species,[3] which remain capable of binding to transition metals.[6]

Despite phosphines being considered excellent ligands in organometallic chemistry, few phosphine-stabilized germylenes have been isolated to date. The first one, **A**, was prepared by Du Mont et al. in 1981,[7] and more recently some Ge(II)halide complexes, **B**, with diphosphine ligands were isolated.[8] An original complex, **C**, featuring two Ge centers in two formal oxidation states was characterized in the solid state,[9] and the intramolecular phosphine-stabilized germylene **D** was isolated two years ago (Figure 1).[10] To the best of our knowledge, the ligand properties of these stabilized germylenes were not studied, and since we have recently prepared a phosphine-stabilized chloro-germylene **1a** (Scheme 1),[11] we were interested in testing its potential as a ligand for transition metals. Indeed, the peculiar structure of **1a**, featuring a chloro substituent (easy to substitute) and a phosphine ligand (versatile soft Lewis base), should allow an easy modulation of the electronic and steric properties of this original ligand. Herein, we report the reactivity of [$Rh_2(\mu\text{-}Cl)_2(COD)_2$] with two different phosphine-stabilized germylenes **1a**,**b**.

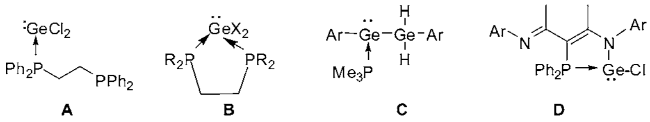
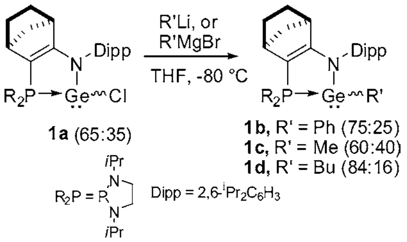


Figure 1. Phosphine-stabilized germylenes.

Scheme 1. Synthesis of Phosphine-Stabilized Germylenes



EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Phosphine-stabilized chloro-germylene **1a** was prepared according to a published method.[11] Dimer complex [$Rh_2(\mu\text{-}Cl)_2(COD)_2$] was purchased from

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Strem Chemicals. The elemental analysis was performed (C, H, N) on a model EA1108 Fisons elemental analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with either Bruker Avance-300 or Avance-500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million relative to $\mathrm{Me_4Si}$ as an external standard. ^{31}P NMR chemical shifts are expressed in parts per million relative to 85% $\mathrm{H_3PO_4}$.

Synthesis of Phosphine-Stabilized Phenyl-Germylene 1b. To a THF solution (20 mL) of **1a** (1.5 g, 2.73 mmol), at −80 °C, was slowly added phenyl lithium (1.58 mL, 1.8 M in hexane, 2.86 mmol). The solution was slowly warmed to room temperature and stirred for 2 h. The ^{31}P NMR spectroscopy indicated the quantitative formation of the new phenyl-substituted germylene **1b** as a mixture of two diastereomers (75/25; δ 80.5 and 75.6). All volatiles were removed in vacuo, and the product was extracted twice with pentane. The major diastereomer of **1b** was obtained in pure form as pale yellow crystals, suitable for an X-ray diffraction analysis, from a concentrated pentane solution at −30 °C (0.72 g, 45%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.56 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 0.90 (d, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 0.91 (overlapped with the methyl signal, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 0.92 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 0.93 (d, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.04 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.09 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3iPr}}$), 0.91 (brs, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 1.17 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.32−1.41 (m, 2H, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$), 1.46 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.55 (m, 1H, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$), 1.69 (m, 1H, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$), 2.48−2.69 (m, 5H, 2 $\mathrm{PNCH_2}$, $\mathrm{PCCH_{bridgehead}}$), 2.88 (m, 1H, $\mathrm{NCCH_{bridgehead}}$), 3.00 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.41 (m, 1H, $\mathrm{PNCH_{iPr}}$), 3.78 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.95 (m, 1H, $\mathrm{PNCH_{iPr}}$), 6.96−7.36 (m, 3H, $\mathrm{H_{Ar}}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 19.9 (d, $^{3}J_{\mathrm{PC}}$ = 0.5 Hz, $\mathrm{CH_{3PNiPr}}$), 20.4 (d, $^{3}J_{\mathrm{PC}}$ = 0.93 Hz, $\mathrm{CH_{3PNiPr}}$), 20.7 (d, $^{3}J_{\mathrm{PC}}$ = 4.5 Hz, $\mathrm{CH_{3PNiPr}}$), 21.3 (d, $^{3}J_{\mathrm{PC}}$ = 7.7 Hz, $\mathrm{CH_{3PNiPr}}$), 23.4 (s, $\mathrm{CH_{3iPr}}$), 24.4 (s, $\mathrm{CH_{3iPr}}$), 24.8 (s, $\mathrm{CH_{3iPr}}$), 25.5 (d, $^{4}J_{\mathrm{PC}}$ = 1.6 Hz, $\mathrm{CH_{2CbridgeheadCN}}$), 26.0 (d, J_{PC} = 2.5 Hz, $\mathrm{CH_{3iPr}}$), 27.8 (s, $\mathrm{CH_{iPr}}$), 28.5 (s, $\mathrm{CH_{iPr}}$), 30.2 (d, $^{3}J_{\mathrm{PC}}$ = 2.3 Hz, $\mathrm{CH_{2CbridgeheadCP}}$), 38.9 (d, $^{2}J_{\mathrm{PC}}$ = 3.0 Hz, $\mathrm{PNCH_2}$), 38.9 (d, $^{2}J_{\mathrm{PC}}$ = 2.8 Hz, $\mathrm{PNCH_2}$), 41.1 (d, $^{3}J_{\mathrm{PC}}$ = 7.9 Hz, $\mathrm{NCCH_{bridgehead}}$), 43.9 (d, $^{2}J_{\mathrm{PC}}$ = 5.8 Hz, $\mathrm{PNCH_{iPr}}$), 44.1 (d, $^{2}J_{\mathrm{PC}}$ = 11.1 Hz, $\mathrm{PCCH_{bridgehead}}$), 44.3 (d, $^{2}J_{\mathrm{PC}}$ = 12.5 Hz, $\mathrm{PNCH_{iPr}}$), 46.3 (d, $^{3}J_{\mathrm{PC}}$ = 4.0 Hz, $\mathrm{CH_{2bridge}}$), 93.4 (d, J_{PC} = 31.3 Hz, PC=CN), 123.5, 124.0, 126.0 ($\mathrm{CH_{Ar}}$), 126.3 (d, $^{3}J_{\mathrm{PC}}$ = 1.68 Hz, 2C, GeCH_{ortho}), 137.2, 134.6, 134.8 ($\mathrm{CH_{Ar}}$), 140.8 (d, $^{3}J_{\mathrm{PC}}$ = 1.4 Hz, NC_{ipso}), 145.7, 147.1 (NC_{ortho}), 152.0 (d, $^{2}J_{\mathrm{PC}}$ = 6.8 Hz, GeC_{ipso}), 183.8 (d, $^{2}J_{\mathrm{PC}}$ = 37.2 Hz, PC=CN). ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 80.5. Anal. calcd for $\mathrm{C_{33}H_{48}N_3PGe}$: C, 67.16; H, 8.20; N, 7.12. Found: C, 67.47; H, 8.23; N, 7.10.

Synthesis of Phosphine-Stabilized Methyl-Germylene 1c. To a THF solution (20 mL) of **1a** (1.0 g, 1.82 mmol), at −80 °C, was slowly added methyl magnesium bromide (0.64 mL, 3.0 M in dibutyl ether, 1.92 mmol). The solution was slowly warmed to room temperature and stirred for 2 h. All volatiles were removed in vacuo, and the product was extracted twice with pentane. Methyl-germylene **1c** was obtained as a yellow powder from a saturated pentane solution at −30 °C (0.28 g, 30%). The ^{31}P NMR spectroscopy indicated the formation of **1c** as a mixture of two diastereomers (60/40; δ 85.6 and 81.0). **Major diastereomer** (60%), ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.61 (d, $^{3}J_{\mathrm{HP}}$ = 18.2 Hz, 3H, $\mathrm{GeCH_3}$), 0.91 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 0.95 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.02 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.05 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.13 (d, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.15 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.16 (overlapped with the methyl signal, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 1.17 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.36 (m, 2H, $\mathrm{CH_{2CbridgeheadCN}}$), 1.43 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.57 (m, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 1.69 (m, 2H, $\mathrm{CH_{2CbridgeheadCP}}$), 2.44−2.67 (m, 5H, 2 $\mathrm{PNCH_2}$, $\mathrm{PCCH_{bridgehead}}$), 2.88 (brs, 1H, $\mathrm{NCCH_{bridgehead}}$), 3.20 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.53−3.64 (m, 2H, $\mathrm{CH_{iPr}}$, $\mathrm{PNCH_{iPr}}$), 3.77 (m, 1H, $\mathrm{PNCH_{iPr}}$), 7.06−7.09 (m, 3H, $\mathrm{H_{Ar}}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 2.9 (d, $^{2}J_{\mathrm{PC}}$ = 4.6 Hz, $\mathrm{GeCH_3}$), 20.2 (d, $^{3}J_{\mathrm{PC}}$ = 1.6 Hz, $\mathrm{CH_{3PNiPr}}$), 20.4 (d, $^{3}J_{\mathrm{PC}}$ = 1.7 Hz, $\mathrm{CH_{3PNiPr}}$), 20.8 (d, $^{3}J_{\mathrm{PC}}$ = 4.3 Hz, $\mathrm{CH_{3PNiPr}}$), 21.7 (d, $^{3}J_{\mathrm{PC}}$ = 0.9 Hz, $\mathrm{CH_{3PNiPr}}$), 24.4 (s, $\mathrm{CH_{3iPr}}$), 24.6 (s, $\mathrm{CH_{3iPr}}$), 24.7 (s, $\mathrm{CH_{3iPr}}$), 25.5 (d, $^{4}J_{\mathrm{PC}}$ = 1.6 Hz, $\mathrm{CH_{2CbridgeheadCN}}$), 26.3 (d, J_{PC} = 2.6 Hz, $\mathrm{CH_{3iPr}}$), 27.6 (s, $\mathrm{CH_{iPr}}$), 28.2 (s, $\mathrm{CH_{iPr}}$), 30.2 (s, $\mathrm{CH_{2CbridgeheadCP}}$), 39.1 (d, $^{2}J_{\mathrm{PC}}$ = 1.1 Hz, $\mathrm{PNCH_2}$), 39.4 (s, $\mathrm{PNCH_2}$), 40.9 (d, $^{3}J_{\mathrm{PC}}$ = 8.0 Hz, NC*C*$\mathit{H}_{\mathrm{bridgehead}}$), 43.9 (d, $^{2}J_{\mathrm{PC}}$ = 12.0 Hz, $\mathrm{PCCH_{bridgehead}}$), 44.9 (d, $^{2}J_{\mathrm{PC}}$ = 7.8 Hz, $\mathrm{PNCH_{iPr}}$), 44.6 (d, $^{2}J_{\mathrm{PC}}$ = 12.1 Hz, $\mathrm{PNCH_{iPr}}$), 46.9 (d, $^{3}J_{\mathrm{PC}}$ = 4.2 Hz, $\mathrm{CH_{2bridge}}$), 91.0 (d, J_{PC} = 28.2 Hz, PC=CN), 123.4, 123.4, 124.1 (3*s*, 3C, $\mathrm{CH_{Ar}}$), 140.7 (d, $^{3}J_{\mathrm{PC}}$ = 2.5 Hz, NC_{ipso}), 146.6, 147.3 (NC_{ortho}), 185.0 (d, $^{2}J_{\mathrm{PC}}$ = 39.4 Hz, PC=CN). ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 85.6. **Minor diastereomer** (40%), ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.81 (d, $^{3}J_{\mathrm{HP}}$ = 18.4 Hz, 3H, $\mathrm{GeCH_3}$), 0.87 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 0.92 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.01 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.11 (d, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.12 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.17 (overlapped with the methyl signal, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 1.19 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.20 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.36 (m, 2H, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$), 1.42 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.43 (overlapped with the methyl signal, 2H, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$), 1.69 (m, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 2.33 (brs, 1H, $\mathrm{PCCH_{bridgehead}}$), 2.44−2.67 (m, 4H, 2 $\mathrm{PNCH_2}$), 2.78 (brs, 1H, $\mathrm{NCCH_{bridgehead}}$), 3.21 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.38 (m, 1H, $\mathrm{PNCH_{iPr}}$), 3.46 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.94 (m, 1H, $\mathrm{PNCH_{iPr}}$), 7.06−7.09 (m, 3H, $\mathrm{H_{Ar}}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 4.2 (d, $^{2}J_{\mathrm{PC}}$ = 2.7 Hz, $\mathrm{GeCH_3}$), 19.8 (d, $^{3}J_{\mathrm{PC}}$ = 1.5 Hz, $\mathrm{CH_{3PNiPr}}$), 21.2 (d, $^{3}J_{\mathrm{PC}}$ = 1.7 Hz, $\mathrm{CH_{3PNiPr}}$), 21.2 (d, $^{3}J_{\mathrm{PC}}$ = 1.1 Hz, $\mathrm{CH_{3PNiPr}}$), 21.8 (d, $^{3}J_{\mathrm{PC}}$ = 4.1 Hz, $\mathrm{CH_{3PNiPr}}$), 24.2 (s, $\mathrm{CH_{3iPr}}$), 24.9 (s, $\mathrm{CH_{3iPr}}$), 25.0 (s, $\mathrm{CH_{3iPr}}$), 26.0 (s, $\mathrm{CH_{3iPr}}$), 26.2 (d, $^{4}J_{\mathrm{PC}}$ = 1.4 Hz, $\mathrm{CH_{2CbridgeheadCN}}$), 27.43 (s, $\mathrm{CH_{iPr}}$), 28.3 (s, $\mathrm{CH_{iPr}}$), 30.2 (s, $\mathrm{CH_{2CbridgeheadCP}}$), 38.9 (s, $\mathrm{PNCH_2}$), 39.1 (d, $^{2}J_{\mathrm{PC}}$ = 1.9 Hz, $\mathrm{PNCH_2}$), 40.7 (d, $^{3}J_{\mathrm{PC}}$ = 7.2 Hz, NC*C*$\mathit{H}_{\mathrm{bridgehead}}$), 43.3 (d, $^{2}J_{\mathrm{PC}}$ = 13.5 Hz, $\mathrm{PCCH_{bridgehead}}$), 43.9 (d, $^{2}J_{\mathrm{PC}}$ = 7.4 Hz, $\mathrm{PNCH_{iPr}}$), 44.4 (d, $^{2}J_{\mathrm{PC}}$ = 11.1 Hz, $\mathrm{PNCH_{iPr}}$), 48.6 (d, $^{3}J_{\mathrm{PC}}$ = 2.7 Hz, $\mathrm{CH_{2bridge}}$), 91.5 (d, J_{PC} = 23.5 Hz, PC=CN), 123.8, 125.9, 126.0 ($\mathrm{CH_{Ar}}$), 141.6 (d, $^{3}J_{\mathrm{PC}}$ = 4.7 Hz, NC_{ipso}), 146.0, 146.3 (NC_{ortho}), 187.3 (d, $^{2}J_{\mathrm{PC}}$ = 41.2 Hz, PC=CN). ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 81.0.

Synthesis of Phosphine-Stabilized Butyl-Germylene 1d. To a THF solution (20 mL) of **1a** (1.0 g, 1.82 mmol), at −80 °C, was slowly added *n*-butyl lithium (1.20 mL, 1.6 M in hexane, 1.92 mmol). The solution was slowly warmed to room temperature and stirred for 2 h. All volatiles were removed in vacuo, and the product was extracted twice with pentane. Butyl-germylene **1d** was obtained as a yellow powder from a saturated pentane solution at −30 °C (0.36 g, 35%). The ^{31}P NMR spectroscopy indicated the formation of **1d** as a mixture of two diastereomers (84/16; δ 85.7 and 80.9). **Major diastereomer** (84%), ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.86 (t, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_{3Bu}}$), 0.98 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.06 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.13 (d, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.15 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3PNiPr}}$), 1.21 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.24 (overlapped with the methyl signal, 2H, $\mathrm{GeCH_2}\mathit{CH}_2{}^{\mathrm{n}}{}_{\mathrm{Bu}}$), 1.25 (overlapped with the methyl signal, 1H, 1/2 $\mathrm{CH_{2bridge}}$), 1.26 (d, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.33 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.38−1.45 (m, 3H, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$, $\mathit{CH}_2\mathrm{CH}_3{}^{\mathrm{n}}{}_{\mathrm{Bu}}$), 1.51 (d, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, 3H, $\mathrm{CH_{3iPr}}$), 1.52 (overlapped with the methyl signal, 2H, 1/2 $\mathrm{CH_{2CbridgeheadCN}}$, 1/2 $\mathrm{GeCH_2{}^{n}{}_{Bu}}$), 1.54−1.64 (m, 3H, 1/2 $\mathrm{CH_{2bridge}}$, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$, 1/2 $\mathrm{GeCH_2{}^{n}{}_{Bu}}$), 1.77 (m, 1H, 1/2 $\mathrm{CH_{2CbridgeheadCP}}$), 2.54−2.65 (m, 3H, $\mathrm{PNCH_2}$, $\mathrm{PCCH_{bridgehead}}$), 2.69−2.80 (m, 2H, $\mathrm{PNCH_2}$), 2.96 (brs, 1H, $\mathrm{NCCH_{bridgehead}}$), 3.29 (sept, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.56−3.65 (m, 1H, $\mathrm{PNCH_{iPr}}$), 3.76 (sept, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 1H, $\mathrm{CH_{iPr}}$), 3.91−4.00 (m, 1H, $\mathrm{PNCH_{iPr}}$), 7.13−7.17 (m, 3H, $\mathrm{H_{Ar}}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 13.9 (s, $\mathrm{CH_3{}^{n}{}_{Bu}}$), 19.1 (d, $^{2}J_{\mathrm{PC}}$ = 4.1 Hz, $\mathrm{GeCH_2{}^{n}{}_{Bu}}$), 20.1 (d, $^{3}J_{\mathrm{PC}}$ = 1.5 Hz, $\mathrm{CH_{3PNiPr}}$), 20.4 (d, $^{3}J_{\mathrm{PC}}$ = 1.5 Hz, $\mathrm{CH_{3PNiPr}}$), 20.7 (d, $^{3}J_{\mathrm{PC}}$ = 4.2 Hz, $\mathrm{CH_{3PNiPr}}$), 21.7 (d, $^{3}J_{\mathrm{PC}}$ = 7.1 Hz, $\mathrm{CH_{3PNiPr}}$), 24.3 (s, $\mathrm{CH_{3iPr}}$), 24.4 (s, $\mathrm{CH_{3iPr}}$), 24.8 (s, $\mathrm{CH_{3iPr}}$), 25.5 (d, $^{3}J_{\mathrm{HP}}$ = 1.3 Hz, 3H, $\mathrm{GeCH_2CH_2{}^{n}{}_{Bu}}$), 26.1 (d, J_{PC} = 2.7 Hz, $\mathrm{CH_{3iPr}}$), 26.4 (s, $\mathrm{CH_{2CbridgeheadCN}}$), 27.5 (s, $\mathrm{CH_{iPr}}$), 28.2 (s, $\mathrm{CH_{iPr}}$), 30.1 (d, $^{4}J_{\mathrm{HP}}$ = 10.2 Hz, 3H, $\mathrm{CH_2CH_3{}^{n}{}_{Bu}}$), 30.3 (d, $^{3}J_{\mathrm{PC}}$ = 1.8 Hz,$\mathrm{CH_{2CbridgeheadCP}}$), 39.0 (d, $^{2}J_{\mathrm{PC}}$ = 2.5 Hz, $\mathrm{PNCH_2}$), 39.2 (d, $^{2}J_{\mathrm{PC}}$ = 1.5 Hz, $\mathrm{PNCH_2}$), 40.9 (d, $^{3}J_{\mathrm{PC}}$ = 7.8 Hz, $\mathrm{NCCH_{bridgehead}}$), 43.8 (d, $^{2}J_{\mathrm{PC}}$ = 10.7 Hz, $\mathrm{PCCH_{bridgehead}}$), 43.8 (d, $^{2}J_{\mathrm{PC}}$ = 7.2 Hz, $\mathrm{PNCH_{iPr}}$), 44.6 (d, $^{2}J_{\mathrm{PC}}$ = 12.8 Hz, $\mathrm{PNCH_{iPr}}$), 48.73 (d, $^{3}J_{\mathrm{PC}}$ = 3.8 Hz, $\mathrm{CH_{2bridge}}$), 90.1 (d, J_{PC} = 29.4 Hz, PC=CN), 123.3, 124.1, 125.8 ($\mathrm{CH_{Ar}}$), 141.0 (d, $^{3}J_{\mathrm{PC}}$ = 2.1 Hz, NC_{ipso}), 146.1, 146.5 (NC_{ortho}), 183.8 (d, $^{2}J_{\mathrm{PC}}$ = 38.6 Hz, PC=CN). ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 85.7. **Minor**

diastereomer (16%), ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.87 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_{3Bu}), 0.98 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_{3PNiPr}), 1.06 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH_{3PNiPr}), 1.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH_{3PNiPr}), 1.15 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_{3PNiPr}), 1.22 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_{3iPr}), 1.24 (overlapped with the methyl signal, 2H, $GeCH_2\mathit{CH}_{2Bu}$), 1.25 (overlapped with the methyl signal, 1H, 1/2 $CH_{2bridge}$), 1.26 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_{3iPr}), 1.33 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.38–1.45 (m, 3H, 1/2 $CH_{2CbridgeheadCN}$, CH_2CH_{3Bu}), 1.51 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_{3iPr}), 1.52 (overlapped with the methyl signal, 2H, 1/2 $CH_{2CbridgeheadCN}$, 1/2 $GeCH_2{}^{n}{}_{Bu}$), 1.54–1.64 (m, 2H, 1/2 $CH_{2CbridgeheadCP}$, 1/2 $GeCH_{2Bu}$), 1.76–185 (m, 2H, 1/2 $CH_{2CbridgeheadCP}$, 1/2 $CH_{2bridge}$), 2.44 (brs, 1H, $PCCH_{bridgehead}$), 2.54–2.65 (m, 2H, $PNCH_2$), 2.69–2.80 (m, 2H, $PNCH_2$), 2.88 (brs, 1H, $NCCH_{bridgehead}$), 3.29 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1H, CH_{iPr}), 3.56–3.65 (m, 1H, $PNCH_{iPr}$), 3.76 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1H, CH_{iPr}), 3.91–4.00 (m, 1H, $PNCH_{iPr}$), 7.13–7.17 (m, 3H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ 13.9 (s, $CH_{3\ Bu}$), 19.3 (d, $^{2}J_{PC}$ = 2.1 Hz, $GeCH_{2Bu}$), 19.8 (d, $^{3}J_{PC}$ = 1.4 Hz, CH_{3PNiPr}), 20.1 (d, $^{3}J_{PC}$ = 1.5 Hz, CH_{3PNiPr}), 21.2 (d, $^{3}J_{PC}$ = 6.4 Hz, CH_{3PNiPr}), 21.4 (d, $^{3}J_{PC}$ = 3.1 Hz, CH_{3PNiPr}), 24.4 (s, CH_{3iPr}), 24.7 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 25.6 (d, $^{3}J_{HP}$ = 1.3 Hz, 3H, $GeCH_2CH_2{}^{n}{}_{Bu}$), 26.2 (d, J_{PC} = 2.7 Hz, CH_{3iPr}), 26.8 (s, $CH_{2CbridgeheadCN}$), 27.4 (s, CH_{iPr}), 28.26 (s, CH_{iPr}), 30.1 (d, $^{3}J_{PC}$ = 0.9 Hz,$CH_{2CbridgeheadCP}$), 30.6 (d, $^{4}J_{HP}$ = 9.8 Hz, 3H, $CH_2CH_3{}^{n}{}_{Bu}$), 39.0 (d, $^{2}J_{PC}$ = 2.5 Hz, $PNCH_2$), 39.2 (d, $^{2}J_{PC}$ = 1.5 Hz, $PNCH_2$), 40.9 (d, $^{3}J_{PC}$ = 7.8 Hz, $NCCH_{bridgehead}$), 43.4 (d, $^{2}J_{PC}$ = 13.5 Hz, $PCCH_{bridgehead}$), 43.9 (d, $^{2}J_{PC}$ = 6.4 Hz, $PNCH_{iPr}$), 44.7 (d, $^{2}J_{PC}$ = 11.3 Hz, $PNCH_{iPr}$), 48.9 (d, $^{3}J_{PC}$ = 3.0 Hz, $CH_{2bridge}$), 92.0 (d, J_{PC} = 30.2 Hz, PC═CN), 123.4, 123.9, 126.1 (CH_{Ar}), 141.6 (d, $^{3}J_{PC}$ = 5.2 Hz, NC_{ipso}), 145.9, 147.3 (NC_{ortho}), 186.8 (d, $^{2}J_{PC}$ = 40.2 Hz, PC═CN). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ 80.9. Anal. calcd for $C_{31}H_{52}N_3PGe$: C, 65.28; H, 9.19; N, 7.37. Found: C, 65.60; H, 9.21; N, 7.40.

Synthesis of Metallacycle 3a. To a THF solution (7 μL) of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (30.0 mg, 0.062 mmol) was added, at RT, **1a** (66 mg, 0.121 mmol), and the reaction mixture was stirred for 2 h. Crystals suitable for an X-ray diffraction analysis were obtained from a saturated THF solution at −30 °C (62.0 mg, 65%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.71 (d, J_{HH} = 8.2 Hz, 1H, 1/2 $CH_{2bridge}$), 1.15 (d, J_{HH} = 6.5 Hz, 3H, CH_{3PNiPr}), 1.18 (d, J_{HH} = 6.7 Hz, 3H, CH_{3PNiPr}), 1.17 (overlapped with the methyl signal, 1H, 1/2 $CH_{2bridge}$), 1.27 (d, J_{HH} = 6.9 Hz, 3H, CH_{3iPr}), 1.29 (d, J_{HH} = 6.9 Hz, 3H, CH_{3iPr}), 1.33 (d, J_{HH} = 6.4 Hz, 3H, CH_{3PNiPr}), 1.45 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.48 (d, J_{HH} = 6.4 Hz, 3H, CH_{3PNiPr}), 1.55 (m, 3H, $CH_{2CbridgeheadCP}$, 1/2 $CH_{2CbridgeheadCN}$), 1.69 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.68 (overlapped with the methyl signal, 1H, 1/2 $CH_{2CbridgeheadCN}$), 1.76–2.11 (m, 8H, $4CH_{2COD}$), 2.53 (m, 1H, $PCCH_{bridgehead}$), 2.58–2.66 (m, 2H, $PNCH_2$), 2.77–2.85 (m, 3H, $NCCH_{bridgehead}$, $PNCH_2$), 3.26 (m, 1H, $PNCH_{iPr}$), 3.70 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 4.13 (sep, J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 4.30 (m, 1H, $PNCH_{iPr}$), 4.80, 4.91 (2xbrs, 2H, $CH{=}CH_{COD}$), 5.45, 5.79 (2xbrs, 2H, $CH{=}CH_{COD}$), 7.17–7.28 (m, 3H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ 21.6 (d, $^{3}J_{PC}$ = 5.4 Hz, CH_{3PNiPr}), 22.0 (d, $^{3}\ J_{PC}$ = 5.5 Hz, CH_{3PNiPr}), 22.4 (d, $^{3}J_{PC}$ = 2.5 Hz, CH_{3PNiPr}), 22.9 (d, $^{3}J_{PC}$ = 6.0 Hz, CH_{3PNiPr}), 24.6 (s, CH_{3iPr}), 24.8 (s, CH_{3iPr}), 25.8 (s, CH_{3iPr}), 26.1 (d, $^{4}J_{PC}$ = 1.2 Hz, $CH_{2CbridgeheadCN}$), 28.0 (s, CH_{iPr}), 28.2 (s, CH_{iPr}), 28.3 (s, $CH_{2CbridgeheadCP}$), 29.1 (d, $^{2}J_{RhC}$ = 2.1 Hz, CH_{2COD}), 29.7 (d, $^{2}J_{RhC}$ = 1.8 Hz, CH_{2COD}), 30.6 (d, $^{2}J_{RhC}$ = 3.2 Hz, CH_{2COD}), 30.9 (d, $^{2}J_{RhC}$ = 1.4 Hz, CH_{2COD}), 39.9 (d, $^{2}J_{PC}$ = 1.7 Hz, $PNCH_2$), 42.7 (d, $^{3}J_{PC}$ = 3.6 Hz, $CH_{2bridge}$), 44.9 (d, $^{2}J_{PC}$ = 13.4 Hz, $PNCH_{iPr}$), 45.8 (d, $^{3}J_{PC}$ = 1.7 Hz, $NCCH_{bridgehead}$), 45.9 (d, $^{2}J_{PC}$ = 1.2 Hz, $PNCH_2$), 47.2 (d, $^{2}J_{PC}$ = 6.3 Hz, $PNCH_{iPr}$), 48.2 (d, $^{2}J_{PC}$ = 8.2 Hz, $PCCH_{bridgehead}$), 94.7 (d, J_{RhC} = 8.2 Hz, $HC{=}CH_{COD}$), 96.2 (t, J_{RhC} = 2.7 Hz, $HC{=}CH_{COD}$), 96.4 (d, J_{RhC} = 5.9 Hz, $HC{=}CH_{COD}$), 100.3 (dd, J_{RhC} = 6.2 Hz, $^{2}J_{PC}$ = 10.2 Hz, $HC{=}CH_{COD}$), 105.2 (dd, J_{PC} = 40.3 Hz, $^{2}J_{RhC}$ = 7.3 Hz, PC═CN), 123.3, 124.2, 126.9 (CH_{Ar}), 140.3 (NC_{ipso}), 147.2, 148.8 (NC_{ortho}), 174.6 (d, $^{2}J_{PC}$ = 17.8 Hz, PC═CN). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ 61.7 (d, J_{PRh} = 153.9 Hz).

Synthesis of Rh(I) Complex 2b. To a THF solution (7 μL) of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (30.0 mg, 0.062 mmol) was added, at RT, phenyl-substituted germylene **1b** (71 mg, 0.121 mmol), and the reaction mixture was stirred for 2 h at RT. The ^{31}P NMR spectroscopy indicated the quantitative formation of the new Rh(I) complex **2b** (broad signal at δ 60.3), and the diastereomeric ratio was estimated from the ^{13}C NMR spectrum (65/35). All volatiles were removed in vacuo, and yellow crystals suitable for an X-ray diffraction analysis were obtained from a CH_2Cl_2–Et_2O solution at −30 °C. **Major diastereomer** (65%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.94 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_{3iPr}), 1.03 (d, $^{3}J_{HH}$ = 6.5 Hz, 6H, CH_{3PNiPr}), 1.14 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_{3iPr}), 1.15 (overlapped with the methyl signal, 1H, 1/2 $CH_{2CbridgeheadCP}$), 1.18 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH_{3PNiPr}), 1.44 (m, 4H, $CH_{2bridge}$, 1/2 $CH_{2CbridgeheadCP}$, 1/2 $CH_{2CbridgeheadCN}$), 1.69 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH_{3PNiPr}, $2CH_{3iPr}$), 1.70 (overlapped with the methyl signal, 1H, 1/2 $CH_{2CbridgeheadCN}$), 1.98 (m, 4H, $PNCH_2$), 2.28 (m, 4H, $PNCH_2$), 2.62 (br s, 1H, $PCCH_{bridgehead}$), 2.70 (m, 1H, CH_{iPr}), 2.93 (brs, 1H, $NCCH_{bridgehead}$), 2.98–3.09 (m, 4H, 2 $PNCH_2$), 3.17–3.23 (m, 2H, $PNCH_{iPr}$), 3.29 (m, 1H, CH_{iPr}), 4.96, 5.07 (2xbrs, 4H, $CH{=}CH_{COD}$), 6.96 (m, 5H, H_{Ar}), 7.22 (m, 3H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 20.3 (s, CH_{3PNiPr}), 21.1 (d, $^{3}J_{PC}$ = 2.5 Hz, CH_{3PNiPr}), 21.4 (d, $^{3}J_{PC}$ = 8.6 Hz, CH_{3PNiPr}), 21.8 (d, $^{3}J_{PC}$ = 1.7 Hz, CH_{3PNiPr}), 22.5 (s, CH_{3iPr}), 25.2 (s, CH_{3iPr}), 25.5 (s, CH_{3iPr}), 25.7 (s, CH_{3iPr}), 26.8 (s, CH_{2COD}), 27.4 (s, CH_{2COD}), 27.5 (s, CH_{iPr}), 27.8 (s, CH_{iPr}), 29.0 (s, CH_{2COD}), 29.4 (s, CH_{2COD}), 32.3 (s, $CH_{2CbridgeheadCN}$), 34.8 (s, $CH_{2CbridgeheadCP}$), 39.0 (brs, $PNCH_2$), 40.9 (d, $^{3}J_{PC}$ = 4.6 Hz, $NCCH_{bridgehead}$), 43.9 (d, $^{2}J_{PC}$ = 6.3 Hz, $PNCH_{iPr}$), 44.1 (d, $^{2}J_{PC}$ = 9.6 Hz, $PNCH_{iPr}$), 45.2 (d, $^{2}J_{PC}$ = 9.1 Hz, $PCCH_{bridgehead}$), 46.4 (brs, $CH_{2bridge}$), 63.2 (brs, $HC{=}CH_{COD}$), 65.1 (brs, $HC{=}CH_{COD}$), 91.5 (d, J_{PC} = 51.4 Hz, PC═CN), 98.8 (m, $HC{=}CH_{COD}$), 99.6 (d, J_{RhC} = 7.3 Hz, $HC{=}CH_{COD}$), 123.5, 124.5, 126.3, 126.9, 127.6 (CH_{Ar}), 134.3 (d, $^{3}J_{PC}$ = 6.4 Hz, $GeCH_{\mathit{ortho}}$), 139.7 (s, NC_{ipso}), 140.2 (brs, GeC_{ipso}), 147.4, 147.9 (NC_{ortho}),190.7 (d, $^{2}J_{PC}$ = 32.4 Hz, PC═CN). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 60.3 (br). **Minor diastereomer** (35%), $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 19.4 (d, $^{3}J_{PC}$ = 3.0 Hz, CH_{3PNiPr}), 20.1 (d, $^{3}J_{PC}$ = 6.3 Hz, CH_{3PNiPr}), 20.9 (s, 2C, CH_{3PNiPr}), 22.3 (s, CH_{3iPr}), 25.0 (s, CH_{3iPr}), 26.0 (s, CH_{3iPr}), 26.1 (s, CH_{3iPr}), 28.0 (s, CH_{iPr}), 28.1 (s, CH_{iPr}), 29.4 (s, CH_{2COD}), 29.7 (s, CH_{2COD}), 30.5 (s, CH_{2COD}), 31.0 (s, $CH_{2CbridgeheadCN}$), 31.1 (s, CH_{2COD}), 35.9 (s, $CH_{2CbridgeheadCP}$), 37.0 (d, $^{2}J_{PC}$ = 7.1 Hz, $PNCH_2$), 37.9 (d, $^{2}J_{PC}$ = 6.2 Hz, $PNCH_2$), 39.5 (d, $^{3}J_{PC}$ = 3.7 Hz, $NCCH_{bridgehead}$), 45.0 (d, $^{2}J_{PC}$ = 8.1 Hz, $PNCH_{iPr}$), 46.4 (brs, $CH_{2bridge}$), 47.2 (d, $^{2}J_{PC}$ = 9.2 Hz, $PCCH_{bridgehead}$), 47.5 (d, $^{2}J_{PC}$ = 7.7 Hz, $PNCH_{iPr}$), 60.2 (d, J_{RhC} = 13.3 Hz, $HC{=}CH_{COD}$), 67.2 (d, J_{RhC} = 13.7 Hz, $HC{=}CH_{COD}$), 90.0 (d, J_{PC} = 52.6 Hz, PC═CN), 97.1 (d, J_{RhC} = 8.1 Hz, $HC{=}CH_{COD}$), 97.5 (d, J_{RhC} = 6.1 Hz, $HC{=}CH_{COD}$), 123.9, 124.1, 128.0, 128.1, 128.6 (CH_{Ar}), 134.3 (d, $^{3}J_{PC}$ = 6.4 Hz, 2C, $GeCH_{\mathit{ortho}}$), 139.7 (s, NC_{ipso}), 140.0 (brs, GeC_{ipso}), 146.2, 146.6 (NC_{ortho}), 192.6 (d, $^{2}J_{PC}$ = 32.4 Hz, PC═CN). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 60.3 (br).

Synthesis of Dimethylbutadiene Cycloadduct 4. To a C_6D_6 solution (0.5 mL) of **1c** (50 mg, 0.095 mmol), at room temperature, was added 2,3-dimethyl-1,3-butadiene (21.4 μL, 0.189 mmol). The solution was warmed at 65 °C for 72 h. All volatiles were removed in vacuo, and the product was obtained as yellow oil and was analyzed without any further purification. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): the most representative signals δ 0.48 (brs, 3H, $GeCH_3$), 1.47 (brs, 3H, CH_3vinyl), 1.47 (brs, 1H, 1/2CH_2vinyl), 1.66 (brs, 3H, CH_3vinyl), 1.70 (brs, 3H, 3/2CH_2vinyl). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ 1.1 (s, $GeCH_3$), 19.2 (s, 2C, CH_3vinyl), 22.0 (d, $^{3}J_{PC}$ = 15.2 Hz, 2C, CH_{3PNiPr}), 22.2 (d, $^{3}J_{PC}$ = 10.6 Hz, CH_{3PNiPr}), 22.8 (d, $^{3}J_{PC}$ = 11.8 Hz, CH_{3PNiPr}), 23.1 (s, CH_{3iPr}), 23.3 (s, CH_{3iPr}), 23.4 (s, CH_{3iPr}), 23.5 (s, CH_{3iPr}), 25.9 (s, $CH_{2CbridgeheadCN}$), 27.6 (s, CH_{iPr}), 27.7 (s, CH_{iPr}), 28.6 (s, 3C, $CH_{2CbridgeheadCP}$, CH_2vinyl), 43.7 (d, $^{2}J_{PC}$ = 1.6 Hz, $PCCH_{bridgehead}$), 44.3 (d, $^{3}J_{PC}$ = 3.7 Hz, $CH_{2bridge}$), 44.8 (d, $^{2}J_{PC}$ = 22.6 Hz, $PNCH_{iPr}$), 49.4 (d, $^{2}J_{PC}$ = 8.7 Hz, $PNCH_2$), 49.7 (d, $^{2}J_{PC}$ = 15.0 Hz, $PNCH_{iPr}$), 50.1 (d, $^{2}J_{PC}$ = 6.7 Hz, $PNCH_2$), 51.4 (d, $^{3}J_{PC}$ = 22.1 Hz, $NCCH_{bridgehead}$), 106.6 (d, J_{PC} = 33.0 Hz, PC═CN), 123.1, 123.3, 126.3 (CH_{Ar}), 129.9, 130.0 (brs, 2C, C═C), 137.1 (s, 2C, NC_{ortho}), 147.2 (brs, NC_{ipso}), 158.9 (d, $^{2}J_{PC}$ = 5.5 Hz, PC═CN). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ 84.5.

Crystallographic Studies. Data for compounds **1a** and **1b** were collected on a Bruker-AXS SMART APEX II diffractometer at 193(2) K, with graphite-monochromated Mo Kα radiation (wavelength =

Table 1. Crystallographic Parameters

	1a	1b	2b	3a
empirical formula	$C_{27}H_{43}ClGeN_3P$	$C_{33}H_{48}GeN_3P$	$C_{41}H_{60}ClGeN_3PRh{\cdot}0.5(CH_2Cl_2)$	$C_{35}H_{54}Cl_2GeN_3PRh$
fw/g mol^{-1}	548.65	590.30	879.30	794.18
cryst size/mm	0.25 × 0.10 × 0.08	0.25 × 0.15 × 0.10	0.34 × 0.26 × 0.16	0.42 × 0.26 × 0.20
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$Fdd2$
a (Å)	10.3296(5)	18.7398(3)	40.324(10)	32.830(8)
b (Å)	18.4260(9)	16.2976(2)	10.852(2)	39.870(7)
c (Å)	15.6319(7)	10.7861(2)	20.025(5)	11.240(3)
α (deg)	90	90	90	90
β (deg)	98.601(3)	101.610(1)	105.206(6)	90
γ (deg)	90	90	90	90
temperature (K)	193	193	293	293
Mo Kα (Å)	0.71073	0.71073	0.7107	0.7107
vol (Å^3)	2941.8(2)	3226.82(9)	8456(4)	14712(6) Å^3
Z	4	4	8	16
ρ_{calc} (g cm^{-3})	1.239	1.215	1.381	1.434
F(000)	1160.0	1256.0		6576
μ (mm^{-1})	1.205	1.024	1.30	1.48
reflns collected	29957	56460	47358	42901
unique reflns	5537	6542	7927	7482
R_{int}	0.1458	0.0678	0.056	0.037
GOF on F2	0.997	1.021	1.08	1.18
R1 [$I > 2\sigma(I)$]	0.0621	0.0363	0.060	0.031
wR2	0.1999	0.0908	0.135	0.080
residual electron density peaks (eÅ^{-3})	0.418/−0.436	0.543/−0.238	0.66/−0.75	0.60/−0.42

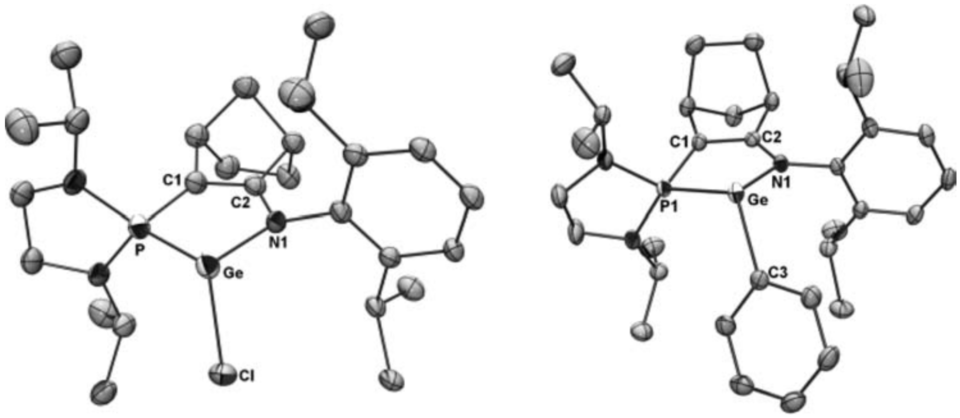


Figure 2. Molecular structure of **1a** (left) and **1b** (right). Thermal ellipsoids represent 30% probability, and H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **1a**: Ge−Cl 2.266(3), N1−Ge 1.989(4), Ge−P 2.474(2), P−C1 1.718(6), C1−C2 1.386(7), C2−N1 1.341(7), Cl−Ge−P 95.23(11), Cl−Ge−N1 96.28(16), N1−Ge−P 83.29(13), Ge−P−C1 95.43(19), P1−C1−C2 116.8(4), C1−C2−N1 126.2(5); for **1b**: Ge−P 2.434(1), Ge−N1 1.993(2), Ge−C3 2.003(2), P−C1 1.724(2); C1−C2 1.387(3), C2−N1 1.343(3), N1−Ge−P 84.69(5), C3−Ge−P 104.43(7), N1−Ge−C3 99.55(9), C2−N1−Ge 114.01(14), N1−C2−C1 124.7(2), C2−C1−P 118.06(17), C1−P−Ge 92.32(8).

0.71073 Å) by using phi and omega scans (see Table 1). The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[12,13] The structures were solved using direct methods, using SHELXS-97,[14] and refined using the least−squares method on F^2.[15] All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. Data for complexes **2b** and **3a** were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a with a Mercury CCD detector using monochromated Mo (Kα) radiation (λ = 0.71070 Å). An empirical absorption correction (multiscan) was applied using the package CrystalClear.[16] The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-PLUS package.[17] Hydrogen atoms on C and N atoms were placed at fixed positions using the HFIX instruction. All of the H atoms were refined with isotropic displacement parameters set to 1.2−1.5 × U_{eq} of the attached atom. In the crystal structure of **2b** a dichloromethane molecule was found disordered. Attempts were made to model this disorder or split it into two positions but were unsuccessful. A PLATON/SQUEEZE routine was used to correct the data for the presence of disordered solvent.[18] A potential solvent volume of 582.7 Å^3 was found. The stoichiometry of the solvent was calculated to be approximately 0.5 molecule of dichloromethane per formula unit, which results in a total of 179 electrons per unit cell. This molecule was used to calculate expected molecular weight, DXcalc and F(000).

Theoretical Calculations. All structures were optimized using DMol^3.[19] This DFT based program allows us to determine the relative stability of all studied species on the basis of their electronic structure. The calculations were performed using the Kohn−Sham Hamiltonian with the Perdew−Wang 1991 gradient correction[20] and the double-ζ

plus (DNP) numerical basic set.[19] The utilization of the numerical basics sets combined with DFT allows the program to obtain a high accuracy by keeping a relatively low computational cost, compared with ab initio methods. DMol[3] calculates variational self-consistent solutions to the density functional theory (DFT) equations. The solutions to these equations provide the molecular electron densities, which can be integrated among the atomic volume (defined by the interatomic surfaces and/or the van der Waals envelope) in order to obtain the Bader charge on each atom of the system.[21]

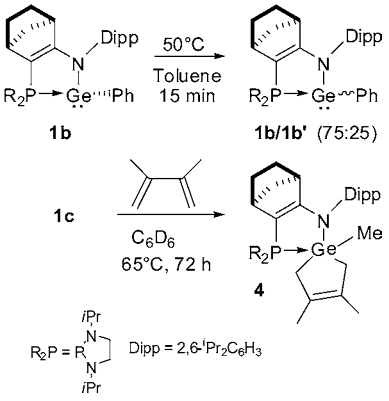
■ RESULTS AND DISCUSSION

Phosphine-Stabilized Germylenes. Phosphine-stabilized chloro-germylene **1a** (mixture of two diastereomers, 65:35) reacts with phenyllithium to yield the new phenyl-substituted germylene **1b** as a mixture of two diastereomers (75:25). Indeed, the ^{31}P NMR spectrum showed two singlet resonances at δ 80.5 and 75.6. Similarly, methyl- and butyl-substituted germylenes **1c** and **1d** were prepared by the reaction of **1a** with one equivalent of MeMgBr or *n*BuLi, respectively. Both were obtained as mixtures of diastereomers as indicated by the ^{31}P NMR spectroscopy: **1c** (δ 85.6 and 81.0, 60:40), **1d** (δ 85.7 and 80.9, 84:16) (Scheme 1).

A diastereoselective crystallization led to the isolation of the major diastereomer of **1b**, which was obtained as yellow crystals from a saturated *n*-pentane solution, at −30 °C. Its structure, unambiguously established by an X-ray diffraction analysis, showed a strongly pyramidalized germanium center ($\Sigma_{Ge\alpha}° =$ 288.6°) and coordination of the phosphine ligand to the germanium atom with a P−Ge distance of 2.434 Å, similar to that observed for phosphine-stabilized chlorogermylene **1a** [2.474(2) Å] and in the range of the previously reported phosphine−germylene compounds (Figure 2).[8−10]

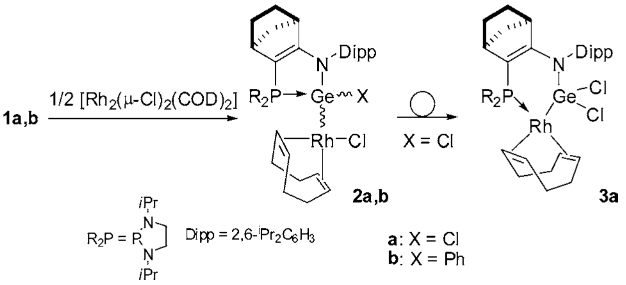
Upon heating a toluene solution of the isolated isomer of **1b** at 50 °C for 15 min, a slow and clean isomerization was observed leading to the initial mixture of diastereomers (75:25) as indicated by the ^{31}P NMR analysis (Scheme 2). The inversion at the trigonal pyramidal germanium center could be rationalized either by a vertex-inversion mechanism or more likely by a P−Ge bond dissociation−Ge−N bond rotation. In order to check the lability of this bond, phosphine-stabilized germylene **1c** was reacted with two equivalents of 2,3-dimethylbutadiene, leading to the formation of the corresponding [4 + 1] cycloadduct **4**, which was obtained as only one diastereomer in good agreement with the occurrence of a dynamic kinetic resolution. The NMR data are very similar to those reported in the case of silicon analogue [4 +1] cycloadduct.[22]

Scheme 2. Isomerization of 1b



Phosphine−Germylene−Rhodium Complexes. The reaction of chloro-germylene derivative **1a** with dimer complex [$Rh_2(\mu\text{-}Cl)_2(COD)_2$] in THF at room temperature, monitored by ^{31}P NMR spectroscopy, leads, after 1 h of reaction, to the formation of a mixture of three rhodium complexes: **2a** (δ 49.3, d, J_{PRh} = 24.2 Hz), **2a′** (δ 51.8, d, J_{PRh} = 28.4 Hz), and **3a** (δ 61.9, d, J_{PRh} = 153.8 Hz). After 2 h at RT, complexes **2a** and **2a′** quantitatively transform into the corresponding rhodium metallacycle **3a** (Scheme 3).

Scheme 3. Reaction of 1a,b with [$Rh_2(\mu\text{-}Cl)_2(COD)_2$]



Crystals of complex **3a**, suitable for an X-ray diffraction analysis, were obtained from a concentrated THF solution at −30 °C. The molecular structure of **3a** clearly exhibits a six-membered cycle, in agreement with the migration of a chlorine atom from the rhodium to the germanium center. Complex **3a** shows slightly distorted square planar geometry around the rhodium atom, which may result from the steric bulk of the phosphino-dichlorogermyl ligand. The Rh−P bond length [2.287 Å] compares well with the Rh−P bonds of metallacycle Rh(I) cyclooctadiene phosphine−carbene complexes.[23] Moreover, the structure of **3a** showed a strongly distorted tetrahedral geometry around the germanium atom, as shown by the Cl2−Ge−Cl1 bond angle [98.3°], which is considerably more acute than the N3−Ge−Rh angle [119.9°]. A similar distortion was previously observed in several trichlorogermyl tungsten complexes.[24] The Ge−Rh bond length (2.358) Å) is much shorter than that observed for $Rh(CO)_4-(GePh_3)$ [2.506 Å][25] probably due to a strong rhodium−dichlorogermyl π-back-bonding.

In the case of the phenyl-substituted germylene ligand **1b**, the corresponding Rh(I) complex **2b** is thermally stable, and was isolated, as yellow air-sensitive crystals from a CH_2Cl_2−Et_2O solution at −30 °C. The ^{31}P NMR spectrum of **2b** showed only one broad singlet resonance at δ 60.3, shifted toward higher field than that observed for the free ligand **1b** (δ 80.5), probably as consequence of the direct coordination of the germylene fragment. Variable temperature ^{31}P NMR measurements (−80 °C − 35 °C) showed no change in the resolution of the spectrum preventing the evaluation of the diastereomeric ratio. In contrast, the ^{13}C NMR spectrum clearly indicated that this Rh(I) complex **2b** was obtained as a mixture of two diastereomers (estimated ratio: 65/35).

The structure of **2b** was unambiguously confirmed by an X-ray diffraction analysis, which clearly shows the σ-coordination of the germylene to rhodium center (Figure 3). Complex **2b** presents a strongly distorted tetrahedral geometry around the germanium atom with a slightly larger N1−Ge−C3 angle (102.64°) than that in **1b** (99.6°), probably due to the change

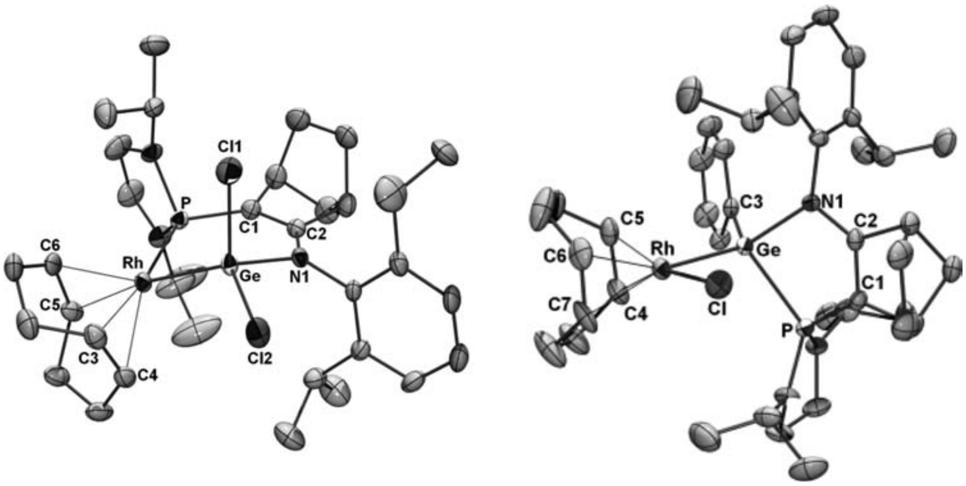


Figure 3. Molecular structure of **3a** (left) and **2b** (right). Thermal ellipsoids represent 30% probability, and H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **3a**: Rh−P 2.2865(12), Rh−Ge 2.3575(6), Ge−Cl1 2.2114(13), Ge−Cl2 2.2316(12), Ge−N1 1.882(3), N1−C2 1.372(5), C1−C2 1.395(6), P−C1 1.764(4); Cl1−Ge−Cl2 98.32(6), N1−Ge−Rh 119.93(10), N1−Ge−Cl2 100.65(11), N1−Ge−Cl1 101.56(10), Cl2−Ge−Rh 119.65(4), Cl1−Ge−Rh 113.19(4), P−Rh−Ge 87.46(3); for **2b**: Ge−Rh 24499(8), Ge−P 2.3943(14), Ge−C3 1.967(5), Ge−N1 1.956(4), N1−C2 1.348(6), C1−C2 1.379(7), P−C1 1.733(5); Cl−Rh−Ge 93.09(5), C3−Ge−Rh 117.75(14), N1−Ge−C3 102.64(19), C3−Ge−P 109.04(15).

of coordination number of the germanium atom. The Ge−P and Ge−C3 bond lengths [2.3943 and 1.967 Å] in **2b** are slightly shorter than in **1b** [Ge−P = 2.434 and Ge−C3 = 2.003 Å]; these differences may be ascribable to the decreasing p character of these bonds as a consequence of the coordination of Rh on the germanium atom. The Ge−Rh bond length in **2b** [2.4499 Å] is slightly longer than that observed for **3a**.

Theoretical Studies. As already mentioned, **2b** is thermally stable compared to **2a**, and no isomerization was observed upon heating at 50 °C for 4 h. With the aim to better explain the experimental results and to gain more information on the electronic properties of both free germylenes and rhodium complexes, DFT calculations have been performed (Table 2).

Table 2. Selected Bond Lengths (Å), Atomic Charge (q), and Electron Density (ρ) at the BCP (in a.u.) Calculated for 1a,b and 2a,b

	q_{Ge}	q_P	q_{Rh}	ρ_{Ge-P}	d_{Ge-P}
1a	+0.56	+1.96		0.067	2.518
1b	+0.75	+1.90		0.068	2.459
2a	+0.71	+1.99	+0.81	0.076	2.460
2b	+0.91	+1.97	+0.37	0.075	2.448

The structures of **1a,b** and **2a,b** were optimized using Dmol^3.[19] Calculations reproduce the same trend experimentally observed, showing a P−Ge bond length slightly shorter for **1b** and **2b** compared with **1a** and **2a**. A Bader's topological analysis of the electron density showed that the density values at the bond critical points (BCP) of the Ge−P bonds are similar in all cases, indicating a similar covalent character of these bonds. Nevertheless, the calculated charges on the P, Ge, and Rh atoms show that the charge deficiency on the Ge atom in **1a** and **2a** is almost 0.2 au lower compared to **1b** and **2b**, respectively, while the electron deficiency for the rhodium atom in **2a** is around 0.5 au higher than that for **2b**. Thus, the high electron deficiency at the rhodium atom in **2a** probably induces the phosphine migration from Ge to Rh center to generate a highly reactive pentacoordinated rhodium−germylene complex, which isomerizes into complex **3**, via the migration of the chlorine atom from the rhodium to the germanium.

■ SUMMARY

We have successfully synthesized the first Ge(II)−Rh(I) complexes featuring a Rh−Cl bond using the original phosphine-stabilized germylene ligands. Of particular interest, the stability of the resulting complexes depends strongly on the electron donating character of germylene fragment, which can be modulated by the nature of the germylene substituent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Theoretical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: baceired@chimie.ups-tlse.fr, eocando@ivic.gob.ve.

Notes

The authors declare no competing financial interest.

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