

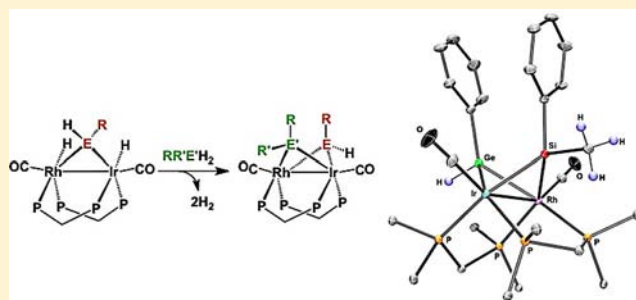
# Mixed Bis( $\mu$ -silylene) and ( $\mu$ -Silylene)/( $\mu$ -Germylene) Complexes Involving the Rh/Ir Metal Combination: Nature of the Si...Si Interactions in the Bis( $\mu$ -silylene) Species

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## Supporting Information

**ABSTRACT:** A series of mixed bis( $\mu$ -silylene) complexes of rhodium and iridium  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHR})(\mu\text{-SiR}^1\text{R}^2)(\text{dppm})_2]$  ( $\text{R} = \text{R}^1 = \text{R}^2 = \text{Ph}$  (**4**);  $\text{R} = \text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Cl}$  (**5**);  $\text{R} = \text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$  (**6**);  $\text{R} = 3,5\text{-C}_6\text{H}_3\text{F}_2$ ,  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$  (**7**);  $\text{R} = 3,5\text{-C}_6\text{H}_3\text{F}_2$ ,  $\text{R}^1 = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$ ,  $\text{R}^2 = \text{H}$  (**8**)) have been synthesized by the reaction of the silylene-bridged dihydride complexes,  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHR})(\text{dppm})_2]$  (**1**,  $\text{R} = \text{Ph}$ ; **2**,  $\text{R} = \text{C}_6\text{H}_3\text{F}_2$ ), with a number of secondary or primary silanes ( $\text{Ph}_2\text{SiH}_2$ ,  $\text{PhClSiH}_2$ ,  $\text{PhMeSiH}_2$ ,  $\text{C}_6\text{H}_2\text{Me}_3\text{SiH}_3$ ). The influence of substituents and  $\pi$ -stacking interactions on the Si...Si distance (determined by X-ray crystallography) in this series and the implications regarding the nature of the Si...Si interactions are discussed. A series of novel ( $\mu$ -silylene)/( $\mu$ -germylene) complexes,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-GePh}_2)(\text{dppm})_2]$  (**9**) and  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiR}^1\text{R}^2)(\mu\text{-GeHPh})(\text{dppm})_2]$  ( $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$  (**11**);  $\text{R}^1 = \text{R}^2 = \text{Ph}$  (**12**);  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$  (**13**)), have also been synthesized by reaction of the silylene-bridged dihydride complex,  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHPh})(\text{dppm})_2]$  (**1**), with 1 equiv of diphenylgermane and by reaction of the germylene-bridged dihydride complex,  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-GeHPh})(\text{dppm})_2]$  (**3**), with 1 equiv of the respective silanes. These complexes have been characterized by multinuclear NMR spectroscopy and X-ray crystallography.



## INTRODUCTION

Bimetallic complexes containing bridging silicon- or germanium-containing units comprise an important class of compounds in organo-transition-metal chemistry,<sup>1</sup> being implicated in E–E (E = Si, Ge)<sup>2</sup> and E–C bond formation.<sup>2b,3</sup> In addition, recent investigations have demonstrated the use of bridging silylene and germylene groups in generating unique Si- and Ge-containing clusters,<sup>4</sup> including unusual examples containing planar arrays of mutually bonded late transition metals.<sup>4b,d</sup> From the perspective of Si–Si bond formation, there has been significant interest in the incorporation of more than one bridging  $\text{SiR}_2$  unit (both R groups can be the same or different) in multimetallic complexes,<sup>2b,e–g,5</sup> involving both early and late transition metals, although those involving late transition metals are in the majority.<sup>1</sup> For complexes having the  $\text{M}_2(\text{SiR}_2)_2$  framework, two major structural classes have emerged in which this  $\text{M}_2\text{Si}_2$  core is either planar and diamond-shaped<sup>2b–e,6</sup> or folded in a butterfly type arrangement, having the Si atoms in the wing-tips with respect to the M–M bond.<sup>2c,f,3a,7–9</sup> Within the planar “ $\text{M}_2(\text{SiR}_2)_2$ ” class a number of examples have been characterized in which the Si...Si separation is short,<sup>2b,c,3c,6c,d,f</sup> approaching that of a normal Si–Si covalent bond, suggesting a significant degree of bonding between these atoms,<sup>10</sup> while in the butterfly type structures<sup>2c,f,3a,7,9a,c</sup> these interactions, although significantly shorter than normal van der Waals contacts, are generally significantly longer than expected

for a Si–Si bond, leading to ambiguity regarding the exact nature of these interactions.

In the butterfly type  $\text{M}_2(\text{SiR}_2)_2$  structures in which the pair of  $\text{SiR}_2$  groups are folded toward each other about the M–M bond, it is tempting to suggest some degree of nascent Si...Si bonding which could, under appropriate conditions, lead to coupling of the  $\text{SiR}_2$  fragments. Although related studies involving two or more bridging  $\text{GeR}_2$  units are much less common, the many similarities in the chemistry of Si and Ge<sup>1a</sup> suggest that related  $\text{M}_2(\text{GeR}_2)_2$  complexes may also be capable of coupling pairs of  $\text{GeR}_2$  units. Our studies have demonstrated many parallels in the formation of analogous butterfly type “ $\text{RhIr}(\mu\text{-EHR})_2$ ” complexes (E = Si, Ge) in reactions of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with primary silanes<sup>9a</sup> and germanes,<sup>9b</sup> while, like silanes, catalytic dehydrogenative coupling of germanes has been observed using both early<sup>11</sup> and late<sup>12</sup> transition metals, although it has not been established whether germylene groups play a role in these coupling reactions.

With the above ideas in mind we set out to expand the scope of  $\text{M}_2(\mu\text{-ER}_2)_2$  butterfly type complexes by generating a series of such species containing pairs of different  $\mu\text{-ER}_2$  groups, either having different substituents on each silylene unit or having mixed silylene and germylene units. The former group

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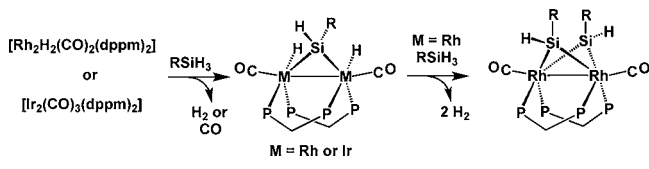
may have potential for the generation of silicon-containing oligomers and polymers having differing sequences of substituents, while the latter could be capable of generating Si/Ge-containing oligomers and polymers. Silicon- and germanium-based polymers are of interest owing to their optical and electronic properties,<sup>13</sup> and for related reasons there has also been significant interest in mixed SiGe-containing oligomers and polymers.<sup>14</sup> Polysilane copolymers, containing different SiR<sub>2</sub> units, are of interest since they can display substantially different physical properties from those of related homopolymers,<sup>13b</sup> allowing flexibility in the modification of polymer properties.

To date, most of the silylene- or germylene-bridged complexes within the butterfly M<sub>2</sub>E<sub>2</sub> class are bridged by the same ER<sub>2</sub> unit (E = Si or Ge). Although a few complexes having [M<sub>2</sub>(μ-ER<sub>2</sub>)(μ-E'R<sub>2</sub>)] or [M<sub>2</sub>(μ-ER<sub>2</sub>)(μ-ER'<sub>2</sub>)] frameworks have been reported, their syntheses are not selective, and they are generally produced as a mixture of products from which the desired species must be isolated.<sup>2b,6g</sup> Two examples of monometallic mixed (silylene)/(germylene) complexes have been reported,<sup>15</sup> but to the best of our knowledge there are no reports describing the *selective* incorporation of two different bridging units into a bimetallic core.

In general, two synthetic approaches have been adopted for the incorporation of pairs of bridging ER<sub>2</sub> units at a bimetallic core: (1) oxidative addition of E–H bonds of primary or secondary silanes or germanes to monometallic precursors, with subsequent dimer formation;<sup>2d,6d,6g,16,17</sup> and (2) oxidative addition of these silanes or germanes at a preorganized bimetallic complex.<sup>3a,6a,7,9,18</sup> The former approach does not appear to be a viable option for the selective incorporation of two different bridging ER<sub>2</sub> groups, being likely to generate mixtures of M<sub>2</sub>(ER<sub>2</sub>)<sub>2</sub>, M<sub>2</sub>(E'R'<sub>2</sub>)<sub>2</sub>, and M<sub>2</sub>(ER<sub>2</sub>)(E'R'<sub>2</sub>) products. However, the second approach appears to be more promising, through the stepwise incorporation of the first ER<sub>2</sub> unit followed by the incorporation of the second such unit, containing either different substituents on each E or different elements (E = Si, Ge), assuming that the first “M<sub>2</sub>(ER<sub>2</sub>)” complex is stable in the absence of excess reagent.

In a previous study on silane activation by a diphosphine-bridged diiridium complex, our group demonstrated that one bridging SiR<sub>2</sub> unit could be incorporated through reactions of an Ir<sub>2</sub> precursor with primary and secondary silanes, to yield [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-SiR')<sub>2</sub>(dppm)<sub>2</sub>] (R = R' = Me, Et, Ph or R = Ph, R' = H; shown for primary silanes in Scheme 1).<sup>8</sup> However,

Scheme 1



incorporation of a second Si-containing unit did not occur owing to the inert nature of these coordinatively saturated mono(silylene)-bridged dihydride products. In contrast, a related dirhodium system, studied by Eisenberg and co-workers, readily incorporates two bridging Si units in reactions involving primary silanes to produce bis(silylene) complexes (Scheme 1),<sup>3a,7</sup> a result of the greater lability of the first silylene-bridged product, [Rh<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-SiHR)(dppm)<sub>2</sub>], which is able to generate the coordinative unsaturation

necessary for reaction with the second silane.<sup>3a,7</sup> Although in this case the reaction could be halted at a mono(silylene)-bridged dirhodium species, subsequent reaction with 1 equiv of a different primary or secondary silane did not lead to the incorporation of the pair of different bridging silylene units, and instead resulted in exchange of the Si-containing units, generating a new mono(silylene)-bridged product.<sup>19</sup> Interestingly, the displacement of bridging silylene groups by germylene groups at a Pt<sub>2</sub> core has also been reported.<sup>17b,20</sup>

Recently we reported a variety of mono- and bis-silylene-bridged and bis-germylene-bridged complexes via the oxidative addition of the appropriate silanes and germanes at a Rh/Ir core.<sup>9</sup> This mixed-metal combination combines the two characteristics of the above homobimetallic compounds, having a labile Rh and a more inert Ir center. This combination appears to give us the “intermediate” reactivity that allows the isolation of monosilylene- or monogermylene-bridged species, which can subsequently react with a second equivalent of the silane or germane precursor, without displacement of the first unit. Although most of this previous work for silane<sup>9a,c</sup> and germane<sup>9b</sup> activation centered on the stepwise addition of the same silane or germane substrates, we reported one example in which two *different* germylene groups were incorporated, using the stepwise activation of the two different germanes.<sup>9b</sup> In the present report we extend this study to the preparation of mixed-bis(silylene)-bridged and (silylene)/(germylene)-bridged species.

An additional goal of this study was to determine the nature of the Si...Si interactions in the butterfly type M<sub>2</sub>(SiR<sub>2</sub>)<sub>2</sub> compounds, which as noted above have Si...Si separations that are intermediate between bonding and nonbonding. Most of the “MM'(μ-ERR')<sub>2</sub>(dppm)<sub>2</sub>” complexes within the butterfly-type class contain at least one aryl group in each bridging ERR' unit, stacked in a parallel arrangement,<sup>3a,7,9</sup> presumably to minimize unfavorable interactions between these aryl groups and the dppm phenyl rings, while maintaining a relatively favorable parallel arrangement of these aryl groups.<sup>21</sup> It is well established that substituents on such aryl groups can have a significant influence on the separation between π-stacked groups, with electron-withdrawing substituents resulting in shorter aryl–aryl separations.<sup>21,22</sup> We were curious about how substituents, either directly on Si or Ge or on the aryl groups, could influence the E...E separations, and wondered whether such influences could shed light on the nature of the E...E interactions. For this part of the study we limit the compounds studied to a series of bis(silylene)-bridged complexes of the type [RhIr(CO)<sub>2</sub>(μ-SiArR)(μ-SiAr'R')(dppm)<sub>2</sub>].

## EXPERIMENTAL SECTION

**General Considerations.** All solvents were dried (using appropriate drying agents), distilled before use, and stored under dinitrogen. Reactions were performed under an argon atmosphere using standard Schlenk techniques. Ph<sub>2</sub>SiH<sub>2</sub> and PhSiH<sub>3</sub> were purchased from Aldrich and Alfa-Aesar, respectively, while Ph<sub>2</sub>SiD<sub>2</sub> and MesSiH<sub>3</sub> (Mes = mesityl) were prepared according to the literature methods.<sup>23a,b</sup> Silanes were dried over CaH<sub>2</sub> and distilled under Ar before use. PhGeH<sub>3</sub> and Ph<sub>2</sub>GeH<sub>2</sub> were synthesized by the reduction of the corresponding chlorides (obtained from Gelest Inc. and Alfa Inorganics, respectively) with LiAlH<sub>4</sub> and kept under argon and subdued light. <sup>13</sup>C-enriched CO (99.4%) and LiAlD<sub>4</sub> were purchased from Cambridge Isotope Laboratories. The compounds [RhIr(CO)<sub>3</sub>(dppm)<sub>2</sub>],<sup>24</sup> [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-SiHPh)(dppm)<sub>2</sub>] (1),<sup>9a</sup> and [RhIr(H)<sub>2</sub>(CO)<sub>2</sub>(μ-GeHPh)(dppm)<sub>2</sub>] (3)<sup>9b</sup> were prepared as previously reported. NMR spectra were recorded on Varian Inova-400,

Varian Inova-500 or Varian VNMRS-500 spectrometers operating at the resonance frequencies for the NMR nuclei as given in the spectral information. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were referenced internally to residual solvent proton signals relative to tetramethylsilane whereas  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were referenced relative to external 85%  $\text{H}_3\text{PO}_4$  and  $\text{CCl}_3\text{F}$  standards, respectively. In the  $^1\text{H}$  NMR spectral results the aromatic protons in the range  $\delta$  8.50–6.20 are not reported. The  $^{13}\text{C}$  NMR resonances for the aryl carbons (in the range  $\delta$  125–135) are also not included. In the spectral data below, the following NMR abbreviations are used: m = multiplet, s = singlet, d = doublet, t = triplet, b = broad. Combinations of these abbreviations are also used. The term “multiplet” is applied to resonances for which the coupling constants cannot be resolved and imply nothing about the order of the spectrum. The elemental analyses were performed by the Microanalytical Laboratory in the department.

**Preparation of Compounds.** a.  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHC}_6\text{H}_3\text{F}_2)(\text{dppm})_2]$  (2). To a slurry of 80 mg (0.069 mmol) of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  in 1 mL of toluene under an atmosphere of Ar in a septum-sealed NMR tube was added 11.5  $\mu\text{L}$  (0.069 mmol) of 3,5- $\text{C}_6\text{H}_3\text{F}_2\text{SiH}_3$  via a microliter syringe followed by an Ar flow through NMR tube by a needle-inlet and needle-outlet. Rapid evolution of CO was observed, accompanied by dissolution of the starting complex followed by the precipitation of compound 2 as a yellow solid within 20 min. The toluene was removed via cannula, and the precipitate was washed with 3 mL of pentane followed by the removal of residual solvents under high vacuum to give analytically pure compound in 72% (59 mg) isolated yield. Anal. Calcd for  $\text{C}_{58}\text{H}_{50}\text{F}_2\text{IrO}_2\text{P}_4\text{RhSi}$ : C, 55.13; H, 3.96. Found: C, 55.43; H, 4.18.  $^{31}\text{P}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 399.8 MHz):  $\delta$  27.5 (Rh–P, bm, 1P), 14.8 (Rh–P, bm, 1P), –9.7 (Ir–P, bm, 1P), –14.9 (Ir–P, bm, 1P).  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 399.8 MHz):  $\delta$  5.43 ( $\text{CH}_2$ , m, 2H), 3.08 ( $\text{CH}_2$ , m, 2H), –9.75 (Rh–H, bm, 1H), –11.20 (Ir–H, bm, 1H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (–40  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 161.8 MHz):  $\delta$  27.6 (Rh–P, dm, 1P),  $^1J_{\text{RhP}} = 97$  Hz), 15.2 (Rh–P, dm, 1P),  $^1J_{\text{RhP}} = 110$  Hz), –9.7 (Ir–P, m, 1P), –15.2 (Ir–P, m, 1P).  $^1\text{H}$  NMR (–40  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 161.8 MHz):  $\delta$  6.48 (Si–H, bs, 1H),  $^1J_{\text{SiH}} = 178$  Hz), 5.48 ( $\text{CH}_2$ , m, 1H), 5.30 ( $\text{CH}_2$ , m, 1H), 3.13 ( $\text{CH}_2$ , m, 1H), 2.84 ( $\text{CH}_2$ , m, 1H), –9.65 (Rh–H, ddm, 1H),  $^2J_{\text{trans PH}} = 143.9$  Hz,  $^1J_{\text{RhH}} = 12$  Hz), –11.25 (Ir–H, dm, 1H),  $^2J_{\text{trans PH}} = 122$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (–40  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 100.5 MHz):  $\delta$  193.3 (Rh–CO, dm, 1C,  $J_{\text{Rh-C}} = 76$  Hz), 180.5 (Ir–CO, m, 1C), 48.7 ( $\text{CH}_2$ , m, 1C), 43.9 ( $\text{CH}_2$ , m, 1C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (–40  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 79.5 MHz, DEPT):  $\delta$  141.2 (m).  $^{19}\text{F}$  NMR (–40  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 376.1 MHz):  $\delta$  –112.4 (m).

b.  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-SiPh}_2)(\text{dppm})_2]$  (4). Under an Ar atmosphere, 70 mg (0.057 mmol) of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHPh})(\text{dppm})_2]$  (1) was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$  in a Schlenk flask followed by the addition of 15.9  $\mu\text{L}$  (0.086 mmol) of  $\text{Ph}_2\text{SiH}_2$ . The reaction mixture was stirred gently for 48 h during which time the yellow solution lightened. NMR spectroscopy of the crude mixture suggested quantitative conversion of complex 1 to 4. The solvent volume was reduced to approximately 0.5 mL under high vacuum. Layering the solution with 2 mL of pentane in an NMR tube yielded light yellow crystals (suitable for X-ray analysis) of compound 4 after 72 h in 56% (45 mg) isolated yield. Anal. Calcd for  $\text{C}_{70}\text{H}_{60}\text{IrO}_2\text{P}_4\text{RhSi}_2$ : C, 59.71; H, 4.26. Found: C, 59.41; H, 4.42.  $^{31}\text{P}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 201.6 MHz):  $\delta$  32.4 (Rh–P, ddd, 1P,  $^1J_{\text{RhP}} = 100$  Hz,  $^2J_{\text{PP}} = 106$  Hz,  $^2J_{\text{PP}} = 32$  Hz), 22.6 (Rh–P, ddd, 1P,  $^1J_{\text{RhP}} = 105$  Hz,  $^2J_{\text{PP}} = 142$  Hz,  $^2J_{\text{PP}} = 32$  Hz), 7.8 (Ir–P, dd, 1P,  $^2J_{\text{PP}} = 106$  Hz,  $^2J_{\text{PP}} = 25$  Hz), –7.9 (Ir–P, dd, 1P,  $^2J_{\text{PP}} = 142$  Hz,  $^2J_{\text{PP}} = 25$  Hz).  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 498.1 MHz):  $\delta$  5.77 (Si–H, m, 1H,  $^1J_{\text{SiH}} = 168$  Hz), 5.00 ( $\text{CH}_2$ , m, 1H), 4.45 ( $\text{CH}_2$ , m, 1H), 2.92 ( $\text{CH}_2$ , m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 100.5 MHz):  $\delta$  200.5 (Rh–CO, dm, 1C,  $^1J_{\text{RhC}} = 76$  Hz), 187.0 (Ir–CO, bs, 1C), 37.5 ( $\text{CH}_2$ , m, 1C), 34.1 ( $\text{CH}_2$ , m, 1C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 79.5 MHz, DEPT):  $\delta$  125.6 ( $\mu\text{-SiPhH}$ , tm,  $^2J_{\text{SiP}} = 70$  Hz), 141.5 ( $\mu\text{-SiPh}_2$ , m).

c.  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-SiCIPh})(\text{dppm})_2]$  (5). Under an atmosphere of Ar, 11.4  $\mu\text{L}$  (0.057 mmol) of  $\text{PhClSiH}_2$  was added to a slurry of 70 mg (0.057 mmol) of 1 in 0.7 mL of toluene in an NMR tube. The mixture was left under an Ar atmosphere overnight at 50  $^\circ\text{C}$ . Light yellow crystals accumulated on the surface of the tube and were

collected and washed with 3 mL of pentane. Evaporation of the residual solvent resulted in analytically pure compound 5 in 40% (31 mg) isolated yield. Redissolving the solid in a minimum volume of toluene and subsequent layering of the toluene solution with pentane in an NMR tube yielded light yellow crystals (suitable for X-ray analysis) of compound 5 after 72 h. Anal. Calcd for  $\text{C}_{64}\text{H}_{55}\text{ClIrO}_2\text{P}_4\text{RhSi}_2$ : C, 56.26; H, 4.02. Found: C, 56.39; H, 4.16.  $^{31}\text{P}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 201.6 MHz):  $\delta$  35.3 (Rh–P, m, 1P), 33.3 (Rh–P, m, 1P), 4.0 (Ir–P, m, 1P), 3.4 (Ir–P, m, 1P).  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 498.1 MHz):  $\delta$  5.50 (Si–H, m, 1H,  $^1J_{\text{SiH}} = 180$  Hz), 5.11 ( $\text{CH}_2$ , m, 1H), 4.42 ( $\text{CH}_2$ , m, 1H), 4.21 ( $\text{CH}_2$ , m, 1H), 2.85 ( $\text{CH}_2$ , m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 100.5 MHz):  $\delta$  200.4 (Rh–CO, dm, 1C,  $^1J_{\text{RhC}} = 74$  Hz), 186.3 (Ir–CO, bs, 1C), 43.5 ( $\text{CH}_2$ , m, 1C), 35.2 ( $\text{CH}_2$ , m, 1C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 79.5 MHz, DEPT):  $\delta$  123.8 ( $\mu\text{-SiPhH}$ , m); the  $\mu\text{-SiCIPh}$  group was not observed.

d.  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-SiMePh})(\text{dppm})_2]$  (6). Under an Ar atmosphere, 100 mg (0.081 mmol) of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHPh})(\text{dppm})_2]$  (1) in a Schlenk flask was dissolved in 5 mL of toluene followed by the addition of 16.8  $\mu\text{L}$  (0.122 mmol) of  $\text{MePhSiH}_2$ . The reaction mixture was stirred under an Ar atmosphere overnight at 50  $^\circ\text{C}$  during which time a white precipitate settled at the bottom of the flask. The supernatant was removed by cannula, and the precipitate was washed with 5  $\times$  3 mL of pentane. Evaporation of the residual solvent resulted in analytically pure compound 6 in 59% (65 mg) isolated yield. Redissolving the solid in a minimum volume of benzene and subsequent layering of the solution with pentane in an NMR tube yielded light yellow crystals (suitable for X-ray analysis) of compound 6 after 48 h. Anal. Calcd for  $\text{C}_{65}\text{H}_{58}\text{IrO}_2\text{P}_4\text{RhSi}_2$ : C, 58.01; H, 4.31. Found: C, 58.03; H, 4.33.  $^{31}\text{P}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 201.6 MHz):  $\delta$  31.4 (Rh–P, m, 1P), 30.2 (Rh–P, m, 1P), 2.4 (Ir–P, m, 1P), –1.3 (Ir–P, m, 1P).  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 498.1 MHz):  $\delta$  5.89 (Si–H, m, 1H,  $^1J_{\text{SiH}} = 169$  Hz), 5.16 ( $\text{CH}_2$ , m, 1H), 4.41 ( $\text{CH}_2$ , m, 1H), 4.09 ( $\text{CH}_2$ , m, 1H), 2.89 ( $\text{CH}_2$ , m, 1H), –0.42 ( $\text{CH}_3$ , m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 100.5 MHz):  $\delta$  200.4 (Rh–CO, d, 1C,  $^1J_{\text{RhC}} = 75$  Hz), 187.5 (Ir–CO, bs, 1C), 47.3 ( $\text{CH}_2$ , m, 1C), 36.8 ( $\text{CH}_2$ , m, 1C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 79.5 MHz, DEPT, gHSQC):  $\delta$  130.7 ( $\mu\text{-SiPhH}$ , tm,  $^2J_{\text{SiP}} = 66$  Hz), 139.2 ( $\mu\text{-SiPhMe}$ , m).

e.  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHC}_6\text{H}_3\text{F}_2)(\mu\text{-SiMePh})(\text{dppm})_2]$  (7). To a slurry of 60 mg (0.047 mmol) of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHC}_6\text{H}_3\text{F}_2)(\text{dppm})_2]$  (2) in 0.6 mL of  $\text{CD}_2\text{Cl}_2$  under an atmosphere of Ar in a septum-sealed NMR tube was added excess  $\text{PhMeSiH}_2$  (26.0  $\mu\text{L}$ ; 0.188 mmol) followed by the gentle heating of the septum-sealed NMR tube at 40  $^\circ\text{C}$  for 12 h in an oil-bath. NMR spectroscopy of the reaction mixture suggested quantitative conversion of 2 to compound 7. Addition of 1 mL of pentane yielded a white precipitate. After the solvent was removed via cannula, the white powder was dried under high vacuum to give the compound in 60% isolated yield. Redissolving the solid in a minimum volume of  $\text{CH}_2\text{Cl}_2$  and subsequent layering of the solution with pentane in an NMR tube yielded light yellow crystals, suitable for an X-ray diffraction study, after 72 h.  $^{31}\text{P}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 201.6 MHz):  $\delta$  31.4 (Rh–P, ddd, 1P,  $^1J_{\text{RhP}} = 106$  Hz,  $^2J_{\text{PP}} = 149$  Hz,  $^2J_{\text{PP}} = 31$  Hz), 29.6 (Rh–P, ddd, 1P,  $^1J_{\text{RhP}} = 100$  Hz,  $^2J_{\text{PP}} = 115$  Hz,  $^2J_{\text{PP}} = 31$  Hz), 1.4 (Ir–P, dd, 1P,  $^2J_{\text{PP}} = 115$  Hz,  $^2J_{\text{PP}} = 24$  Hz), –1.2 (Ir–P, dd, 1P,  $^2J_{\text{PP}} = 149$  Hz,  $^2J_{\text{PP}} = 24$  Hz).  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 498.1 MHz):  $\delta$  5.74 (Si–H, m, 1H,  $^1J_{\text{SiH}} = 173$  Hz), 5.14 ( $\text{CH}_2$ , m, 1H), 4.41 ( $\text{CH}_2$ , m, 1H), 4.09 ( $\text{CH}_2$ , m, 1H), 2.84 ( $\text{CH}_2$ , m, 1H), –0.42 ( $\text{CH}_3$ , m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 100.5 MHz):  $\delta$  200.7 (Rh–CO, d, 1C,  $^1J_{\text{RhC}} = 72$  Hz), 187.0 (Ir–CO, bs, 1C), 47.1 ( $\text{CH}_2$ , m, 1C), 36.8 ( $\text{CH}_2$ , m, 1C), 19.3 ( $\text{CH}_3$ , m, 1C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 79.5 MHz, DEPT):  $\delta$  129.6 (Si–H, m), 139.5 (Si– $\text{CH}_3$ , m).  $^{19}\text{F}$  NMR (27  $^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 376.1 MHz):  $\delta$  –114.0 (m).

f.  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHC}_6\text{H}_3\text{F}_2)(\mu\text{-SiHC}_6\text{H}_2\text{Me}_3)(\text{dppm})_2]$  (8). To a slurry of 50 mg (0.040 mmol) of  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHC}_6\text{H}_3\text{F}_2)(\text{dppm})_2]$  (2) in 0.6 mL of  $\text{CD}_2\text{Cl}_2$  under an atmosphere of Ar in a septum-sealed NMR tube was added 13.0  $\mu\text{L}$  of  $\text{C}_6\text{H}_2\text{Me}_3\text{SiH}_3$  (0.080 mmol) followed by gentle heating at 40  $^\circ\text{C}$  for 12 h in an oil-bath. Addition of 1 mL of pentane yielded a white precipitate. After the solvent was removed via cannula, the white powder was dried under high vacuum

to give analytically pure compound in 54% (30 mg) isolated yield. Anal. Calcd for  $C_{67}H_{60}F_2IrO_4P_4RhSi_5$ : C, 57.08; H, 4.25. Found: C, 57.17; H, 4.33.  $^{31}P\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 201.6 MHz):  $\delta$  29.2 (Rh–P, ddd, 1P,  $^1J_{RhP} = 103$  Hz,  $^2J_{PP} = 130$  Hz,  $^3J_{PP} = 30$  Hz), 24.8 (Rh–P, ddd, 1P,  $^1J_{RhP} = 100$  Hz,  $^2J_{PP} = 130$  Hz,  $^3J_{PP} = 30$  Hz), –1.4 (Ir–P, dd, 1P,  $^2J_{PP} = 130$  Hz,  $^3J_{PP} = 22$  Hz), –3.8 (Ir–P, dd, 1P,  $^2J_{PP} = 130$  Hz,  $^3J_{PP} = 22$  Hz).  $^1H$  NMR (27 °C,  $CD_2Cl_2$ , 498.1 MHz):  $\delta$  5.89 (Si–H, m, 1H,  $^1J_{SiH} = 169$  Hz), 5.84 (Si–H, m, 1H,  $^1J_{SiH} = 190$  Hz), 5.11 ( $CH_2$ , m, 1H), 4.68 ( $CH_2$ , m, 1H), 3.92 ( $CH_2$ , m, 1H), 3.10 ( $CH_2$ , m, 1H), 2.50 (*o*- $CH_3$ , s, 3H), 2.25 (*o*- $CH_3$ , s, 3H), 2.12 (*p*- $CH_3$ , s, 3H).  $^{13}C\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 100.5 MHz):  $\delta$  199.4 (Rh–CO, dm, 1C,  $^1J_{RhC} = 74$  Hz), 185.9 (Ir–CO, s, 1C), 40.1 ( $CH_2$ , m, 1C), 38.5 ( $CH_2$ , m, 1C), 25.6 (*o*- $CH_3$ , m, 1C), 25.4 (*o*- $CH_3$ , m, 1C), 22.3 (*p*- $CH_3$ , m, 1C).  $^{29}Si\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 79.5 MHz, DEPT):  $\delta$  119.6 (Si–H, m), 96.0 (Si–H, m).  $^{19}F$  NMR (27 °C,  $CD_2Cl_2$ , 376.1 MHz):  $\delta$  –114.1 (m).

**g.**  $[RhIr(CO)_2(\mu-SiHPh)(\mu-GePh_2)(dppm)_2]$  (**9**). A 70 mg (0.057 mmol) portion of  $[RhIr(H)_2(CO)_2(\mu-SiHPh)(dppm)_2]$  (**1**) in a Schlenk flask was dissolved in 10 mL of  $CH_2Cl_2$  followed by the addition of 11  $\mu$ L (0.057 mmol) of  $Ph_2GeH_2$ . The reaction mixture was stirred gently for 12 h during which time the yellow solution turned orange. NMR spectroscopy of the crude mixture showed formation of **9** in approximately 90% yield together with a previously reported product  $[RhIr(CO)_2(\mu-GeHPh)(\mu-GePh_2)(dppm)_2]$  (**10**)<sup>9b</sup> in 10% yield. (When compound **1** was reacted with excess (approximately 4 equiv) germane the portion of minor product **10** increased to as high as 25%.) The solvent volume of a 9:1 mixture of these products was reduced to approximately 0.7 mL under high vacuum. Layering the solution with 2 mL of pentane in an NMR tube yielded light yellow cocrystals (suitable for X-ray analysis) of compounds **9** and **10** after 72 h in 3:1 ratio.  $^{31}P\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 201.6 MHz):  $\delta$  35.8 (Rh–P, ddd, 1P,  $^1J_{RhP} = 112$  Hz,  $^2J_{PP} = 142$  Hz,  $^3J_{PP} = 30$  Hz), 24.4 (Rh–P, ddd, 1P,  $^1J_{RhP} = 104$  Hz,  $^2J_{PP} = 138$  Hz,  $^3J_{PP} = 30$  Hz), 7.8 (Ir–P, dd, 1P,  $^2J_{PP} = 112$  Hz,  $^3J_{PP} = 23$  Hz), –7.9 (Ir–P, dd, 1P,  $^2J_{PP} = 138$  Hz,  $^3J_{PP} = 23$  Hz).  $^1H$  NMR (27 °C,  $CD_2Cl_2$ , 498.1 MHz):  $\delta$  5.72 (Si–H, m, 1H,  $^1J_{SiH} = 168$  Hz), 5.12 ( $CH_2$ , m, 1H), 4.42 ( $CH_2$ , m, 1H), 2.98 ( $CH_2$ , m, 1H), 2.94 ( $CH_2$ , m, 1H).  $^{13}C\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 100.5 MHz):  $\delta$  199.8 (Rh–CO, dm, 1C,  $^1J_{RhC} = 73$  Hz), 186.2 (Ir–CO, bs, 1C), 36.8 ( $CH_2$ , m, 1C), 34.5 ( $CH_2$ , m, 1C).  $^{29}Si\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 79.5 MHz, DEPT):  $\delta$  128.7 (Si–H, tm,  $^2J_{SiP} = 70$  Hz).

**h.**  $[RhIr(CO)_2(\mu-SiHPh)(\mu-GeHPh)(dppm)_2]$  (**11**). In a septum-sealed NMR tube, 70 mg (0.055 mmol) of  $[RhIr(H)_2(CO)_2(\mu-GeHPh)(dppm)_2]$  (**3**) was dissolved in 0.7 mL of  $CH_2Cl_2$  under an atmosphere of Ar, followed by the addition of 6.8  $\mu$ L (0.055 mmol) of  $PhSiH_3$ . The reaction mixture slowly changed color from yellow to orange over a period of 12 h. After this period, the solution was transferred to a Schlenk flask via cannula. NMR spectroscopy of the crude products showed 70% formation of complex **11** along with 30% of other unidentified products. Unfortunately, repeated attempts to isolate this complex form the crude mixture did not succeed.  $^{31}P\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 201.6 MHz):  $\delta$  27.3 (Rh–P, ddd, 1P,  $^1J_{RhP} = 104$  Hz,  $^2J_{PP} = 112$  Hz,  $^3J_{PP} = 30$  Hz), 23.0 (Rh–P, ddd, 1P,  $^1J_{RhP} = 118$  Hz,  $^2J_{PP} = 138$  Hz,  $^3J_{PP} = 30$  Hz), 0.7 (Ir–P, dd, 1P,  $^2J_{PP} = 112$  Hz,  $^3J_{PP} = 22$  Hz), –7.2 (Ir–P, dd, 1P,  $^2J_{PP} = 138$  Hz,  $^3J_{PP} = 22$  Hz).  $^1H$  NMR (27 °C,  $CD_2Cl_2$ , 498.1 MHz):  $\delta$  6.20 (Si–H, m, 1H,  $^1J_{SiH} = 168$  Hz), 5.91 (Ge–H, m, 1H), 5.25 ( $CH_2$ , m, 1H), 4.65 ( $CH_2$ , m, 1H), 3.12 ( $CH_2$ , m, 1H), 2.91 ( $CH_2$ , m, 1H).  $^{13}C\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 100.5 MHz):  $\delta$  200.3 (Rh–CO, dm, 1C,  $^1J_{RhC} = 73$  Hz), 186.9 (Ir–CO, bs, 1C), 35.7 ( $CH_2$ , m, 1C), 34.3 ( $CH_2$ , m, 1C).  $^{29}Si\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 79.5 MHz, DEPT):  $\delta$  129.7 (Si–H, tm,  $^2J_{SiP} = 68$  Hz).

**i.**  $[RhIr(CO)_2(\mu-SiPh_2)(\mu-GeHPh)(dppm)_2]$  (**12**). Under an Ar atmosphere, 70 mg (0.055 mmol) of  $[RhIr(H)_2(CO)_2(\mu-GeHPh)(dppm)_2]$  (**3**) in a Schlenk flask was dissolved in 10 mL of  $CH_2Cl_2$  followed by the addition of 15.3  $\mu$ L (0.083 mmol) of  $Ph_2SiH_2$ . The reaction mixture was stirred gently for 48 h during which time the yellow solution lightened slightly. NMR spectroscopy of the crude mixture showed approximately 90% conversion to complex **12** along with 10% unreacted compound **3**. Reduction of the solvent volume to

approximately 1 mL under high vacuum, followed by layering the solution with 3 mL of pentane yielded light yellow crystals (suitable for X-ray analysis) of compound **12** after 72 h in 49% (39 mg) isolated yield. Under refluxing condition in dichloromethane, this reaction required approximately 8–10 h to reach completion. Anal. Calcd for  $C_{70}H_{60}GeIrO_2P_4RhSi_5$ : C, 57.88; H, 4.13. Found: C, 58.19; H, 4.19.  $^{31}P\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 201.6 MHz):  $\delta$  32.4 (Rh–P, ddd, 1P,  $^1J_{RhP} = 98$  Hz,  $^2J_{PP} = 111$  Hz,  $^3J_{PP} = 31$  Hz), 24.4 (Rh–P, ddd, 1P,  $^1J_{RhP} = 115$  Hz,  $^2J_{PP} = 145$  Hz,  $^3J_{PP} = 31$  Hz), 7.8 (Ir–P, dd, 1P,  $^2J_{PP} = 111$  Hz,  $^3J_{PP} = 23$  Hz), –7.9 (Ir–P, dd, 1P,  $^2J_{PP} = 145$  Hz,  $^3J_{PP} = 23$  Hz).  $^1H$  NMR (27 °C,  $CD_2Cl_2$ , 498.1 MHz):  $\delta$  6.19 (Ge–H, m, 1H), 5.00 ( $CH_2$ , m, 1H), 4.50 ( $CH_2$ , m, 1H), 2.98 ( $CH_2$ , m, 1H), 2.91 ( $CH_2$ , m, 1H).  $^{13}C\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 100.5 MHz):  $\delta$  200.2 (Rh–CO, dm, 1C,  $^1J_{RhC} = 73$  Hz), 187.5 (Ir–CO, bs, 1C), 37.5 ( $CH_2$ , m, 1C), 33.4 ( $CH_2$ , m, 1C).

**j.**  $[RhIr(CO)_2(\mu-SiPhMe)(\mu-GeHPh)(dppm)_2]$  (**13**). Under an Ar atmosphere, 70 mg (0.055 mmol) of  $[RhIr(H)_2(CO)_2(\mu-GeHPh)(dppm)_2]$  (**3**) in a Schlenk flask was dissolved in 10 mL of  $CH_2Cl_2$  followed by the addition of 15.1  $\mu$ L (0.11 mmol) of  $MePhSiH_2$ . The reaction mixture was stirred gently for 72 h during which time the yellow solution became orange. NMR spectroscopy of the crude mixture showed approximately 90% conversion to complex **13** along with 10% unreacted compound **3**. Reduction of the solvent volume to approximately 1 mL under high vacuum followed by the slow addition of pentane to a stirring solution of **13** yielded a yellow powder in 53% (41 mg) isolated yield. In refluxing dichloromethane, the reaction was complete in 12 h, but it also produced approximately 20% unidentified products. Single crystals, suitable for an X-ray diffraction study, were obtained after 24 h by layering a concentrated benzene solution (0.5 mL) of **13** with pentane (2.0 mL) in an NMR tube. Anal. Calcd for  $C_{65}H_{58}GeIrO_2P_4RhSi_5$ : C, 56.15; H, 4.17. Found: C, 56.38; H, 4.31.  $^{31}P\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 201.6 MHz):  $\delta$  34.0 (Rh–P, ddd, 1P,  $^1J_{RhP} = 117$  Hz,  $^2J_{PP} = 153$  Hz,  $^3J_{PP} = 30$  Hz), 30.1 (Rh–P, ddd, 1P,  $^1J_{RhP} = 105$  Hz,  $^2J_{PP} = 142$  Hz,  $^3J_{PP} = 30$  Hz), 2.5 (Ir–P, dd, 1P,  $^2J_{PP} = 142$  Hz,  $^3J_{PP} = 20$  Hz), 1.0 (Ir–P, dd, 1P,  $^2J_{PP} = 153$  Hz,  $^3J_{PP} = 20$  Hz).  $^1H$  NMR (27 °C,  $CD_2Cl_2$ , 498.1 MHz):  $\delta$  6.40 (Ge–H, m, 1H), 5.17 ( $CH_2$ , m, 1H), 4.43 ( $CH_2$ , m, 1H), 4.18 ( $CH_2$ , m, 1H), 2.94 ( $CH_2$ , m, 1H).  $^{13}C\{^1H\}$  NMR (27 °C,  $CD_2Cl_2$ , 100.5 MHz):  $\delta$  200.9 (Rh–CO, dm, 1C,  $^1J_{RhC} = 74$  Hz), 187.1 (Ir–CO, bs, 1C), 46.9 ( $CH_2$ , m, 1C), 37.1 ( $CH_2$ , m, 1C), –7.9 ( $CH_3$ , s, 1C).  $^{29}Si\{^1H\}$  (27 °C,  $CD_2Cl_2$ , 79.5 MHz, DEPT):  $\delta$  139.7 (Si–H, tm,  $^2J_{SiP} = 73$  Hz).

**X-ray Data Collection and Structure Determination.** *a. General Considerations.* Single crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane into  $CH_2Cl_2$  (**4**, **7**, **9**, **12**), benzene (**6**, **13**), or toluene (**5**) solutions of the compounds. Data were collected on either a Bruker D8/APEX II CCD diffractometer (**4**, **5**, **6**, **7**, **13**) or Bruker PLATFORM/APEX II CCD (**9**, **12**) diffractometer at –100 °C using Mo  $K\alpha$  radiation.<sup>25</sup> Data were corrected for absorption through the use of Gaussian integration from indexing of the crystal faces. The structures were solved using Patterson location of heavy atoms followed by structure expansion (DIRDIF-2008)<sup>26</sup> (**4**, **12**) or by direct methods (SHELXS-97<sup>27</sup> (**5**, **6**, **7**, **9**, **13**)). Refinement was carried out using the program SHELXL-97.<sup>27</sup> For each complex, the metal atom sites were found to be disordered, and thus were treated as a combination of 50% Ir and 50% Rh sharing the same site. Hydrogen atoms attached to carbons were assigned positions based on the  $sp^2$  or  $sp^3$  hybridization geometries of their parent atoms, and were given isotropic displacement parameters 20% greater than the  $U_{eq}$ 's of their parent carbons. The hydrogen atoms attached to silicon or germanium atoms were located from difference Fourier maps, and their atomic coordinates and thermal parameters were allowed to freely refine. A listing of crystallographic experimental data is provided for all structures as Supporting Information.

*b. Special Refinement Conditions.* **1. Compound 5.** The two solvent toluene molecules were found to be disordered, and were each split into two sets of atom positions, each having an occupancy factor of 0.5. Distances involving the methyl carbons of these molecules were restrained during refinement:  $d(C(10S)–C(11S)) = d(C(20S)–$

$C(21S) = d(C(30S)-C(31S)) = d(C(40S)-C(41S)) = 1.50(1) \text{ \AA}$ ;  $d(C(10S)\cdots C(12S)) = d(C(10S)\cdots C(16S)) = d(C(20S)\cdots C(22S)) = d(C(20S)\cdots C(26S)) = d(C(30S)\cdots C(32S)) = d(C(30S)\cdots C(36S)) = d(C(40S)\cdots C(42S)) = d(C(40S)\cdots C(46S)) = 2.52(1) \text{ \AA}$ . The phenyl rings of these solvent toluene molecules were modeled as idealized regular hexagons with C–C bond lengths of exactly 1.39 Å and C–C–C ring bond angles of exactly 120°.

2. **Compound 7.** One of the two solvent dichloromethane molecules was found to be disordered. One chlorine and one carbon atom of this molecule were split into two positions each, with relative occupancy factors of 0.667 and 0.333. The C–Cl distances within this molecule were restrained to be the same (within 0.03 Å) during refinement.

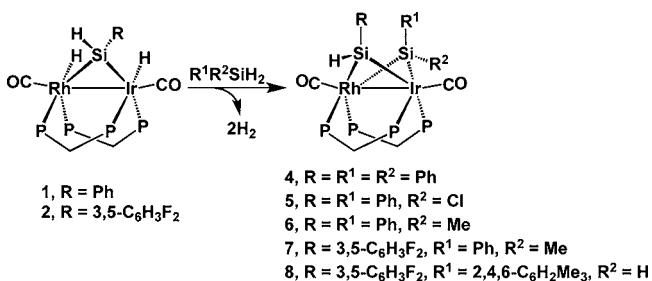
3. **Compound 9.** The atomic position labeled “Si” was refined as a combination of 75% Si and 25% Ge sharing the same site.

4. **Compound 12.** One chlorine atom of the solvent dichloromethane molecule was disordered over two positions, which were refined with relative occupancy factors of 0.8 and 0.2, and with common anisotropic displacement parameters.

## RESULTS AND CHARACTERIZATION OF COMPOUNDS

**a. Mixed Bis( $\mu$ -silylene) Complexes.** Reaction of the silylene-bridged dihydride complexes,  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-SiHR})(\text{dppm})_2]$  (**1**, R = Ph; **2**, R = C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>), with 1 equiv of either secondary or primary silanes (Ph<sub>2</sub>SiH<sub>2</sub>, PhClSiH<sub>2</sub>, PhMeSiH<sub>2</sub>, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>SiH<sub>3</sub>) yields a series of mixed bis-(silylene)-bridged complexes,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHR})(\mu\text{-SiR}^1\text{R}^2)(\text{dppm})_2]$  (R = R<sup>1</sup> = R<sup>2</sup> = Ph (**4**); R = R<sup>1</sup> = Ph, R<sup>2</sup> = Cl (**5**); R = R<sup>1</sup> = Ph, R<sup>2</sup> = Me (**6**); R = 3,5-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>, R<sup>1</sup> = Ph, R<sup>2</sup> = Me (**7**); R = 3,5-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>, R<sup>1</sup> = 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>, R<sup>2</sup> = H (**8**)), by double Si–H bond activation and concomitant reductive elimination of 2 equiv of hydrogen either at ambient temperature (**4** and **5**) or at 40–50 °C (**6**, **7**, **8**) (Scheme 2).

Scheme 2

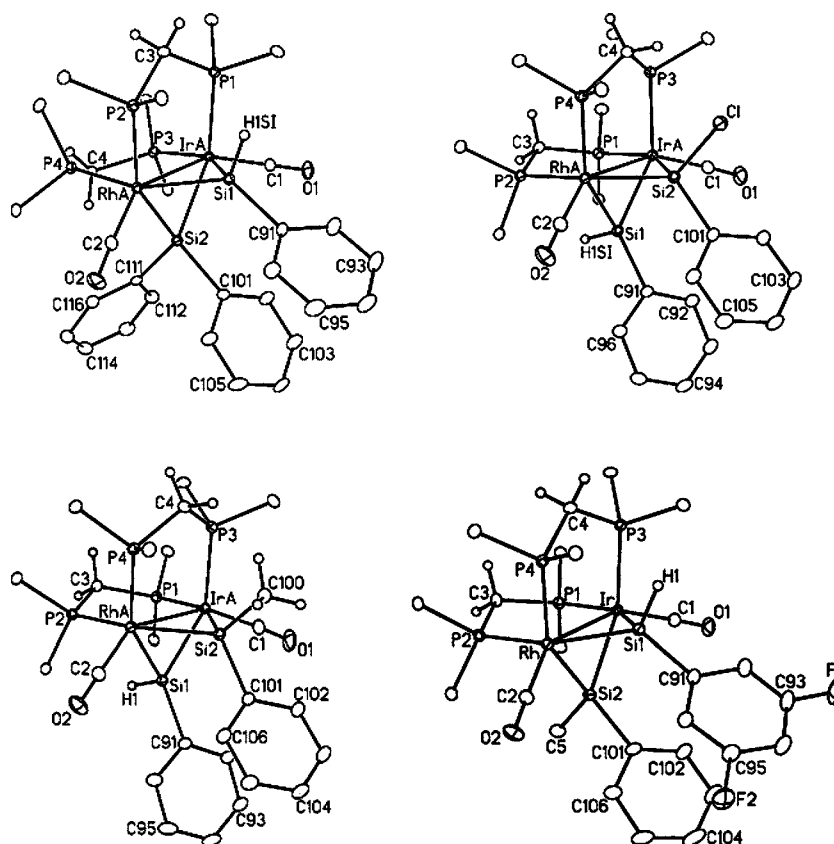


All complexes were characterized by multinuclear NMR spectroscopy and X-ray crystallography (except for complex **8**, the structure of which could not be refined due to unresolved disorder in the crystals).

The NMR spectra of these complexes are all closely comparable, showing four multiplets in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra owing to the chemical inequivalence of all <sup>31</sup>P nuclei. As is the case in related compounds,<sup>9</sup> the two downfield resonances are assigned to Rh-bound <sup>31</sup>P nuclei on the basis of their coupling to <sup>103</sup>Rh. Although for compounds **4**, **7**, and **8** the coupling to Rh (ca. 100 Hz) is clearly resolved from the other couplings, it is not resolved for **5** and **6** but is nevertheless obvious from the greater complexity of these signals owing to the additional Rh coupling. A multiplet is observed for the Si-bound proton of each complex in the <sup>1</sup>H NMR spectrum at between  $\delta$  5.5 and 5.9, displaying <sup>29</sup>Si satellites (<sup>1</sup>J<sub>SiH</sub> ≈ 168–180 Hz), and each resonance collapses to a singlet upon

broadband <sup>31</sup>P decoupling. In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectra two distinct multiplets are observed (with the exception of compound **5** for which the  $\mu$ -SiPhCl group was not detected) at between  $\delta$  96 and 142, as is usually observed for bridging silylene units; these chemical shifts lie intermediate between typical values for silyl groups and terminal silylene units.<sup>1</sup> Incorporation of the different substituents was confirmed by using NMR spectroscopy. For instance, complex **8** displays a multiplet at  $\delta$  –114.1 in the <sup>19</sup>F NMR spectrum corresponding to the fluoroaryl group (presumably a result of accidental equivalence of the two expected fluorine resonances) while in the <sup>1</sup>H NMR spectrum three equal-intensity singlets appear at  $\delta$  2.50, 2.25, and 2.12 for the three mesityl methyl groups. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra display a doublet of multiplets (at ca.  $\delta$  200; <sup>1</sup>J<sub>RhC</sub> ≈ 75 Hz) and a broad singlet (at ca.  $\delta$  187), for the Rh- and Ir-bound carbonyls, respectively. Comparison of the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of these complexes with those of the previously reported bis(silylene)-bridged complexes,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHR})_2(\text{dppm})_2]$  (R = Ph or C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>),<sup>9a</sup> eliminates the possibility that the above reactions produce a mixture of homo-bis(silylene)-bridged products,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHR})_2(\text{dppm})_2]$  and  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiR}^1\text{R}^2)_2(\text{dppm})_2]$ , instead of the single mixed bis(silylene)-bridged products, shown in Scheme 2. In addition, our previous studies<sup>9a</sup> established that bis(silylene)-bridged complexes, in which both silylene fragments are disubstituted, such as  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiR}_2)_2(\text{dppm})_2]$  (R = Ph, or Me), could not be obtained due to the steric demands of the pair of bulky bridging units. Selected spectra for the above species are given as Supporting Information.

The X-ray structures of compounds **4**, **5**, **6**, and **7**, shown in Figure 1, confirm the mixed bis(silylene) formulations for these species. Selected structural parameters for these compounds are given as Supporting Information. All complexes adopt a “cradle-shape” diphosphine arrangement in which these groups are cis at both metals. Each metal has a distorted octahedral geometry, similar to the previously reported dppm-bridged bis( $\mu$ -silylene)<sup>3a,7,9a</sup> and bis( $\mu$ -germylene) complexes.<sup>9b</sup> The metal–metal distances in these complexes (approximately 2.80 Å) are consistent with the presence of a formal metal–metal bond while the nonbonded Si⋯Si distances (2.858(1) Å for **4**, 2.821(1) Å for **5**, 2.8755(8) Å for **6**, and 2.865(1) Å for **7**) are longer than the longest known Si–Si single bond (2.69 Å),<sup>28</sup> although significantly shorter than the sum of the van der Waals radii of two Si atoms (4.20 Å).<sup>29</sup> In all cases, the  $\mu$ -silylene groups are arranged having an aryl ring on each Si parallel and adjacent, having a centroid-to-centroid distance of 3.720 Å for **4**, 3.660 Å for **5**, 3.729 Å for **6**, and 3.552 Å for **7**. These ring separations are within the range 3.3–3.8 Å, typical of  $\pi$ -stacking interactions.<sup>21a</sup> In this series, it is interesting to note that the centroid-to-centroid distance between phenyl rings becomes shorter when electron-withdrawing groups are introduced either on the phenyl ring (compound **7**) or directly on silicon (compound **5**). This is consistent with our previous studies in which we observed a significant decrease in centroid-to-centroid distance (from 3.736 to 3.551 Å) between parallel phenyl rings in bis(silylene)-bridged complexes, upon introduction of electron-withdrawing fluorines on the rings.<sup>9a</sup> In contrast, when an electron-donating group (CH<sub>3</sub>) is introduced on the bridging silylene of compound **6**, the centroid-to-centroid distance is now increased to 3.729 Å. Although the introduction of electron-withdrawing substituents on the phenyl rings significantly decreases the separation between



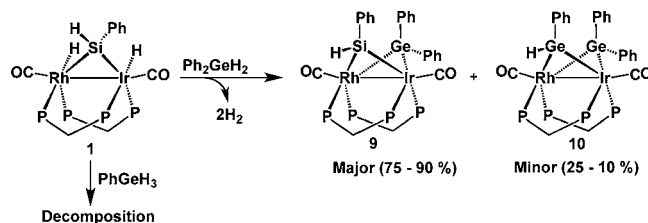
**Figure 1.** Perspective view of complexes **4** (top left), **5** (top right), **6** (bottom left), and **7** (bottom right) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown arbitrarily small but are not shown for the aryl groups. For the dppm phenyl groups, only the ipso carbons are shown. For all complexes the Rh and Ir metals are disordered, but the structures refined well with each metal site having a 50% occupancy of Rh and Ir.

the parallel aryl rings, the distance between the two corresponding silicon atoms changes surprisingly little, and in fact in one case increases slightly, as will be discussed in detail later.

**b. Mixed ( $\mu$ -Silylene)/( $\mu$ -Germylene) Complexes.** In an attempt to obtain mixed ( $\mu$ -silylene)/( $\mu$ -germylene) species the phenylsilylene-bridged compound **1** was first reacted with 1 equiv of phenylgermane; however, this reaction led to the formation of several unidentified products, as evident in the  $^{31}\text{P}\{\text{H}\}$  NMR spectrum. This behavior is reminiscent of our earlier reaction of the corresponding mono(phenylgermylene)-bridged Rh/Ir dihydride complex (**3**) with 1 equiv of phenylgermane, which also resulted in decomposition.<sup>9b</sup> However, the reaction of **1** with 1 equiv of diphenylgermane successfully yields the first mixed silylene- and germylene-bridged complex,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-GePh}_2)(\text{dppm})_2]$  (**9**), in approximately 90% yield along with 10% of the previously reported bis(germylene)-bridged complex,  $[\text{RhIr}(\text{CO})_2(\mu\text{-GeHPh})(\mu\text{-GePh}_2)(\text{dppm})_2]$  (**10**)<sup>9b</sup> (Scheme 3). When the reaction is carried out in the presence of excess  $\text{Ph}_2\text{GeH}_2$ , the yield of **10** increases (up to 25%) with a corresponding drop in the yield of **9**. The mechanism for formation of **10** is not clear, although the addition of excess (4 equiv)  $\text{Ph}_2\text{GeH}_2$  to a 10:1 mixture of **9** and **10** leaves the ratio unchanged, indicating that **10** is not produced through the intermediacy of **9**; instead, it is produced by a competing reaction.

Mixed ( $\mu$ -silylene)/( $\mu$ -germylene) complexes can also be prepared by reaction of the monogermylene-bridged complexes

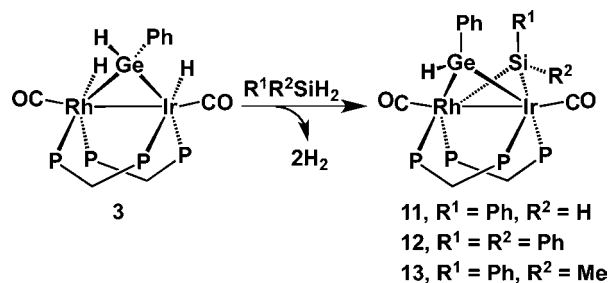
**Scheme 3**



with silanes. For example, the reaction of the phenylgermylene-bridged dihydride complex,  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-GeHPh})(\text{dppm})_2]$  (**3**), with phenylsilane leads to the formation of  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiHPh})(\mu\text{-GeHPh})(\text{dppm})_2]$  (**11**) as the major product (70%) along with some unidentified decomposition products. This is an interesting contrast to the reverse reaction of complex **1** with phenylgermane, noted above, and of the previously reported reaction of **3** with phenylgermane,<sup>9b</sup> both of which lead to decomposition. The reaction of **3** with a series of secondary silanes yields the corresponding series of mixed (silylene)/(germylene)-bridged complexes,  $[\text{RhIr}(\text{CO})_2(\mu\text{-SiR}^1\text{R}^2)(\mu\text{-GeHPh})(\text{dppm})_2]$  ( $\text{R}^1 = \text{R}^2 = \text{Ph}$  (**12**);  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$  (**13**); Scheme 4).

The NMR spectroscopic features and X-ray structures of these ( $\mu$ -silylene)/( $\mu$ -germylene) complexes are similar to those of mixed bis(silylene)-bridged complexes mentioned above. The X-ray structures of complexes **9** (which cocrystallized with **10** in 3:1 ratio), **12**, and **13** are shown in Figure 2, confirming the mixed ( $\mu$ -silylene)/( $\mu$ -germylene) formulation.

Scheme 4



In each case the nonbonded distance between adjacent Ge and Si atoms of the two bridging units (2.9582(5) Å for compound **9**, 2.9255(6) Å for **12**, and 2.9322(7) Å for **13**) is much longer than for a Si–Ge single bond (2.357(4) Å)<sup>30</sup> which appears to preclude any significant interaction between these two atoms; however, these distances are again much shorter than the sum of the van der Waals radii (4.21 Å) of Si and Ge,<sup>29</sup> leaving some doubt about the nature of the Si⋯Ge interactions. As noted for the mixed bis(silylene)-bridged complexes the silicon–germanium nonbonded distance in **13** is again slightly longer than in **12**, presumably due to the presence of electron-donating methyl group in the former.

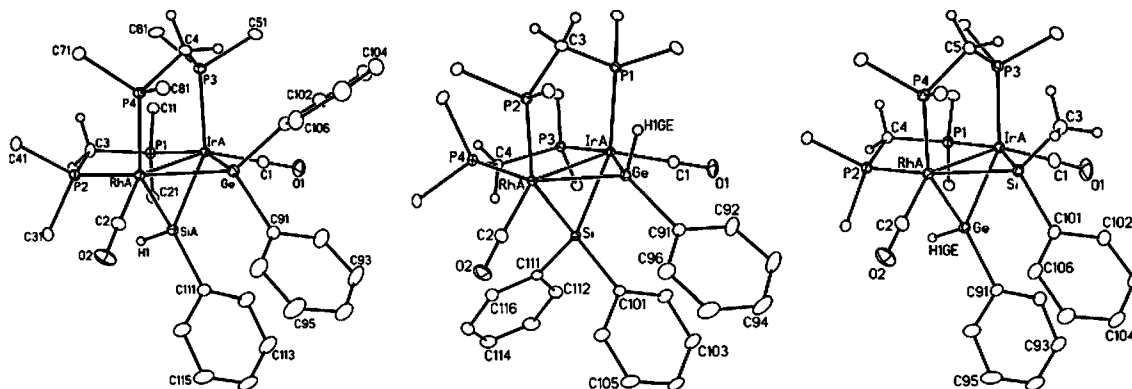
## DISCUSSION

As noted in the Introduction, we had two major goals in this study: (1) to synthesize a series of mixed bis( $\mu$ -silylene) and ( $\mu$ -silylene)/( $\mu$ -germylene) complexes which have potential applications for the coupling of the same elements having different substituents or for the coupling of Si- and Ge-containing units; and (2) to study the influence of different silylene substituents and  $\pi$ -stacked aromatic rings on the Si⋯Si separation in such complexes, in order to obtain information about the nature of the interactions between bridging silylene units.

We were certainly successful in our first goal by taking advantage of stable mono-EHPh-bridged dihydride complexes as precursors, which upon reaction with an equivalent of a different organosilane or an organogermane, yield a series of mixed bis( $\mu$ -silylene) and ( $\mu$ -silylene)/( $\mu$ -germylene) complexes. All of the dibridged complexes reported above are formed either at room temperature over extended periods

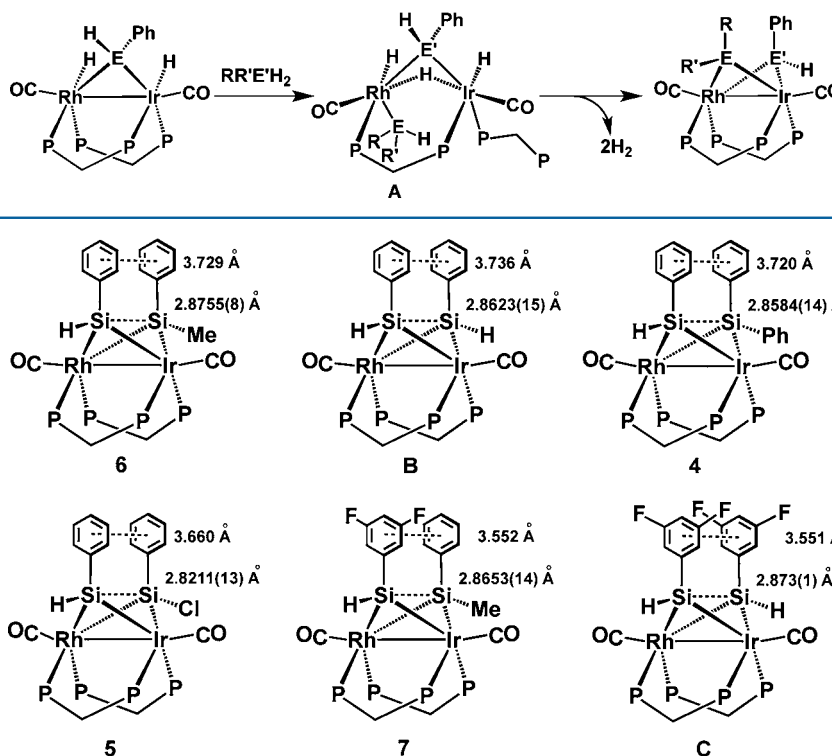
(between 24 and 72 h) or require slightly elevated reaction temperatures. As a consequence, low-temperature studies failed to generate products, so intermediates in their formation could not be observed. However, during the formation of complex **13**, the presence of a small amount (ca. 5%) of an intermediate species was detected in the  $^{31}P\{^1H\}$  NMR spectra, in which four multiplets were observed at  $\delta$  25.2, 7.1, –6.1, and –28.2. Only the downfield peak displays Rh–P coupling while the most upfield peak corresponds to the free end of a pendent diphosphine, as has been previously observed in the formation of bis( $\mu$ -silylene) and bis( $\mu$ -germylene) complexes.<sup>3a,9a,b</sup> Although this pendent diphosphine species has not been characterized owing to its low abundance, we propose a structure like **A** as shown in Scheme 5, analogous to intermediates previously characterized by us in related chemistry.<sup>9a,b</sup>

The coordinative unsaturation necessary for reaction of the monosilylene or monogermylene precursor with the second silane or germane can result either from dissociation of one arm of a diphosphine or by reductive elimination of a silylene or germylene and a hydride unit from the more labile Rh center to give an unsaturated Ir-bound silyl or germyl species. Certainly, in previous studies on related RhIr compounds, hydride exchange between Rh, Ir and Si/Ge<sup>9</sup> was found to be facile, as was also the case for the dirhodium analogues.<sup>3a,7</sup> Although hydride exchange was not pursued in detail in this study, we did observe that reaction of the mono(germylene)-bridged complex **3** with  $Ph_2SiD_2$  results in the evolution of both HD and  $H_2$  gas, as seen in the  $^1H$  NMR spectrum along with the partial incorporation of deuterium in the germanium-bound proton position during the formation of the ( $\mu$ -silylene)/( $\mu$ -germylene) complex (**12**), again suggesting a dynamic exchange process between these metal-bound hydrides and the germanium-bound protons. The ease of the hydride exchange, noted above and in previous studies,<sup>3a,7,9</sup> leads us to suggest that the reversible elimination of a silylene/hydride (or germylene/hydride) unit at one metal gives rise to the necessary coordinative unsaturation for reaction with additional substrate, which is subsequently facilitated by dissociation of the Rh-bound end of a diphosphine to ease the crowding within the inner coordination spheres of the metals. This proposal is supported by the failure of the phenylsilylene-bridged dirhodium dihydride analogue to react with a second equivalent of



**Figure 2.** Perspective view of complex **9** (left), **12** (middle), and **13** (right) showing atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown arbitrarily small and are not shown for phenyl rings. For the dppm phenyl groups, only the ipso carbons are shown. For all complexes, Rh(A) and Ir(A) were refined at 50% occupancy. For compound **9**, the SiA position was refined with a site occupancy of  $Si_{0.75}Ge_{0.25}$  (see Experimental Section).

Scheme 5



**Figure 3.** Representations of the bis( $\mu$ -silylene) complexes showing the separation between the parallel aryl rings and the pair of Si atoms. Complexes B and C were reported previously.<sup>9a</sup>

phenylsilane, combined with the absence of hydride exchange involving this less labile  $\text{Ir}_2$  system.<sup>8</sup>

As noted above another of our goals was to understand how the silylene substituents influence the  $\text{Si}\cdots\text{Si}$  separation between the two bridging units, and to determine whether the variation in this separation with different substituents could disclose something about the nature of the  $\text{Si}\cdots\text{Si}$  interactions. In the three mixed bis(silylene)-bridged complexes (4, 5, and 6) studied, all contain a common monosubstituted bridging-phenylsilylene unit ( $\mu$ -SiPhH) and a different disubstituted bridging-silylene unit ( $\mu$ -SiPhX; X = Ph (4), Cl (5), and Me (6); see Figure 3). A comparison of the  $\text{Si}\cdots\text{Si}$  separations involving compounds 4, 5, 6 and a previously reported bis(phenylsilylene)-bridged complex (complex B in Figure 3) shows that decreasing the electron-donating nature of the Si-bound substituents gives rise to a decrease in the  $\text{Si}\cdots\text{Si}$  separation. As shown in Figure 3, the  $\text{Si}\cdots\text{Si}$  separation decreases in the following order: X = Me (6);  $\text{Si}\cdots\text{Si}$  = 2.8755(8) Å > X = H (B);  $\text{Si}\cdots\text{Si}$  = 2.8623(15) Å > X = Ph (4);  $\text{Si}\cdots\text{Si}$  = 2.8584(14) Å > X = Cl (5);  $\text{Si}\cdots\text{Si}$  = 2.8211(13) Å. This decrease in  $\text{Si}\cdots\text{Si}$  separation (ca. 0.055 Å) as the electron-withdrawing nature of the Si–X bond increases is accompanied by a corresponding decrease (0.069 Å) in the separation between  $\pi$ -stacked aryl rings.

The influence of ring substituents can be seen in two sets of compounds. Compounds B and C<sup>9a</sup> differ only in the aryl substituents, with B having parallel unsubstituted phenyl rings, while C has electronegative fluorines in the meta positions of both rings. The two fluorine substituents give rise to a substantial decrease in separation between the ring centroids (by ca. 0.18 Å), while resulting in a slight increase (by 0.01 Å) in the  $\text{Si}\cdots\text{Si}$  separation. Compounds 6 and 7, each having a

methyl substituent on one Si, can also be compared, differing only in the aryl substituents (this time on only one ring). Again fluorine substitution gives rise to a significant decrease in centroid-to-centroid distance of ca. 0.18 Å, but has little effect on the  $\text{Si}\cdots\text{Si}$  separation which decreases marginally (0.01 Å). The decrease in separation between  $\pi$ -stacked aryl rings upon substitution by electron withdrawing groups is well established.<sup>21</sup> However, we were surprised to observe that this closer approach of the aryl rings has little effect on the  $\text{Si}\cdots\text{Si}$  separation. If the close approach of the pair of Si atoms in these bis-silylene-bridged compounds (in which the  $\text{Si}\cdots\text{Si}$  separations are significantly less than van der Waals separations) were a consequence of nascent Si–Si bonding, we would expect that reducing the repulsions between their attached  $\pi$ -stacked aryl groups, through the introduction of electronegative substituents on these groups, would allow the Si atoms to optimize their mutual bonding, leading to a shortening of the Si–Si separation. The observed insensitivity of this separation to fluorine substitution on the  $\pi$ -stacked rings indicates that closer approach of the pairs of Si atoms is not inhibited by van der Waals repulsion between the parallel aryl groups, and further suggests that mutual attraction by weak bonding interactions between the Si atoms is minimal.

On the basis of the above argument we suggest that the significant change in  $\text{Si}\cdots\text{Si}$  separation upon changing the Si-bound substituents (in the series 6, B, 4, and 5) might be attributed to a decrease in electron density at Si upon substitution by more electron-withdrawing groups (Me < H < Ph < Cl), leading to less van der Waals repulsion between these centers, and therefore shorter separation. The accompanying decrease in aryl–aryl separation with the introduction of electron-withdrawing substituents on Si is presumably a



result of accompanying withdrawal of electron density from these  $\pi$ -stacked rings leading to less repulsion between these groups. Both effects, resulting from direct substitution on Si, are most evident in **5**, having the very electronegative chlorine substituent.

In conclusion, we have developed a protocol for the synthesis of a wide variety of mixed bis( $\mu$ -silylene) complexes with different substituents on each bridging element and have extended this protocol for the synthesis of a series of novel ( $\mu$ -silylene)/( $\mu$ -germylene) complexes of Rh and Ir. To our knowledge this latter accomplishment represents the first example of the selective incorporation of two different bridging elements of group 14 into a bimetallic core. We have also been able to obtain crystallographic evidence of substituent effects on the Si...Si separation in the bis( $\mu$ -silylene) complexes involving substituents directly on Si or on the  $\pi$ -stacked aryl groups. Our conclusion from this part of the study is that the short separation between the silicon atoms is not the result of any nascent bonding interaction, but instead represents a close van der Waals separation enforced by the steric demands involving the bulky dpmm groups.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Tables of crystallographic experimental details and selected bond distances and angles for compounds **4**-CH<sub>2</sub>Cl<sub>2</sub>, **5**-2PhMe, **6**-2.5C<sub>6</sub>H<sub>6</sub>, **7**-CH<sub>2</sub>Cl<sub>2</sub>, **9**-CH<sub>2</sub>Cl<sub>2</sub>, **12**-CH<sub>2</sub>Cl<sub>2</sub>, and **13**-5C<sub>6</sub>H<sub>6</sub>. Selected NMR spectra for compounds **4**–**11**. Atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for these compounds in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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