Allenyl to Alkenylcarbyne Tautomerization at the Ru-Si Bond of Ru($\kappa P,P,Si$) Pincer Complexes

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Supporting Information Placeholder

ABSTRACT: The reactions of the dimer $[\text{Ru}(\mu\text{-Cl})\{\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**1**) with 2-methyl-3-butyne-2-ol and 3-chloro-3-methyl-1-butyne are reported. The former stops at the reagent coordination step forming the mononuclear η^2 alkyne complex $[\text{Ru}/\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2]\text{Cl}\{\eta^2\text{-HC}\equiv\text{CC}(\text{OH})\text{Me}_2\}$ (**2**) while the latter sequentially produces the allene derivative $[\text{Ru}(\text{Cl})_2\{\kappa P,P\text{-Si}(\text{Me})(1,2\text{-}\eta\text{-CH}=\text{C}=\text{CMe}_2)(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]$ (**3**) and its alkenylcarbyne isomer $[\text{Ru}/\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2](\text{Cl})_2(\text{C}\equiv\text{CCH}=\text{CMe}_2)$ (**4**). The structures of complexes **3** and **4** indicate that the allenyl fragment that results from the activation of the propargylic chloride uses the Ru-Si bond of the pincer complex to tautomerize into an alkenylcarbyne ligand.

INTRODUCTION

Propargylic alcohols and halides are common sources of unsaturated ligands such as allenylidenes,¹ allenyls and propargyls.² These versatile species can afterwards be transformed into a variety of other organometallics via nucleophilic or electrophilic attacks,^{1,4} or through metal-mediated C-H bond formations and cleavages leading to the migration of hydrogens and C-C multiple bonds along the ligands.⁵ Occasionally, silyl groups have proved to be as competent as hydrogens for these migrations.⁶ Recently, we described that carbene ligands can reversibly insert into the Ru-Si bond of ruthenium complexes coordinating the $\kappa P,P,Si$ pincer $[\text{Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2]$, and that such insertions contribute to improve and diversify the reactivity of the carbenes.⁷ The present work reveals that allenyl ligands can also insert into this Ru-Si bond and use it to tautomerize into alkenylcarbynes, thus showing that ligands other than carbenes can exploit this resource of the $\kappa P,P,Si$ pincer complexes.

RESULTS AND DISCUSSION

Previously,⁷ we reported that the reaction between phenylacetylene and the dimer $[\text{Ru}(\mu\text{-Cl})\{\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**1**) produced the mononuclear vinylidene complex $[\text{Ru}/\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2]\text{Cl}(\text{C}=\text{CHPh})$. Aimed at the preparation of an allenylidene analogue,^{1,8} we reacted **1** with 2-methyl-3-butyne-2-ol, but the reaction stopped at the very initial step giving the η^2 alkyne complex $[\text{Ru}/\kappa P,P,Si\text{-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2]\text{Cl}\{\eta^2\text{-HC}\equiv\text{CC}(\text{OH})\text{Me}_2\}$ (**2**) (Scheme 1). The compound was stable enough to be isolated and characterized, although the alkyne coordination was found to be reversible. Thus, in solvents such as toluene, where **1** is relatively insoluble, the solutions of **2** were observed to partially evolve crystals of the precursor dimer together with the free propargylic alcohol.

The NMR spectra of complex **2** suggest that the pincer ligand coordinates half way between *mer* and *fac* modes. The chemi-

cal equivalence of the two phosphorous in the $^{31}\text{P}\{^1\text{H}\}$ spectrum, typical of *mer* complexes, indicates that chloride and alkyne ligands can coincide in a symmetry (equatorial) plane. In contrast, several signals of the $^{13}\text{C}\{^1\text{H}\}$ spectra corresponding to nuclei coupled to both magnetically inequivalent phosphorous indicate that they are weakly coupled ($^2J_{\text{PP}}$ ca. 9 Hz, see supporting information for details), a typical feature of *fac* isomers. The ability of this pincer ligand to adapt its coordination angles to the size requirements of the other ligands has been previously discussed in closely related complexes.⁷

Scheme 1

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals corresponding to the alkyne moiety of **2** appear at remarkable low fields: δ 7.69 (t, $^3J_{\text{HP}} = 3.0$ Hz), and δ 127.21 (br, CH) and 172.11 (t, $^2J_{\text{CP}} = 12.7$ Hz, C), respectively. Similar anomalous chemical shifts have been recognized in related osmium compounds,⁹ and attributed to the coordination of the alkyne as a four-electron donor to better stabilize otherwise unsaturated complexes. Such a coordination mode is also consistent with the ^1H nOesy NMR spectrum, in which the methyl group at silicon evidences spatial proximity with the alkyne hydrogen but not with the other alkyne substituent, thus suggesting a hindered rotation of this ligand.

In contrast to the behavior of the propargylic alcohol, the chloride analogue 3-chloro-3-methyl-1-butyne was found to surpass the coordination step to give the sequence of reactions shown in Scheme 2.

Scheme 2

The first observable complex in this sequence, the derivative $[\text{Ru}(\text{Cl})_2\{\kappa P, P\text{-Si}(\text{Me})(1,2\text{-}\eta\text{-CH=C=Me}_2)(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]$ (**3**), was isolated as a green solid after 30 minutes of reaction at 243 K. The structure of **3** (Figure 1, above) shows that the alkyne reagent has split into a chloride ligand and an allenyl fragment, which now replaces the former Si-Ru bond as a $\mu\text{-}\kappa\text{C}, \eta^2$ ligand. Given the mild reaction conditions and the inferred structure of the alkyne complex **2** (Scheme 1), a concerted C-Cl bond cleavage / C-Si bond formation directly leading to **3** from a putative η^2 alkyne intermediate appears as a plausible mechanistic possibility. Nevertheless, a more conventional mechanism involving C-Cl oxidative addition¹⁰ and Si-C reductive elimination¹¹ steps seems also likely, as the possibly required propargyl to allenyl tautomerization is generally considered an easy process.²

The structural parameters of the η^2 allene coordination to ruthenium in **3** are within the range found in related complexes.¹² The C(26)-C(27) and C(27)-C(28) bond distances are 1.387(4) and 1.316(3) Å, respectively, and the C(26)-C(27)-C(28) angle is 151.0(3)°. The cleavage of the Ru-Si bond and the functionalization of the silicon also produced readily recognizable changes in the NMR spectra.⁷ The positive ²⁹Si chemical shifts characteristic of the pincer silicon (δ 66.04 for **1** or 59.54 for **2**) become negative after formation of the new Si-C bond (δ -19.61 for **3**). This bond also generates a new chiral center and therefore, whatever the ligand arrangement, chemically inequivalent phosphorous atoms, which now appear in the ³¹P{¹H} spectrum as two doublets displaying a mutual coupling constant of 19.8 Hz. This small constant is also consistent with the P(1)-Ru-P(2) angle of 106.60(3)° found in the solid state structure.

In solution, complex **3** was observed to slowly transform into an isomer containing an allenylcarbyne ligand, $[\text{Ru}\{\kappa P, P, \text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}(\text{Cl})_2(\text{C}\equiv\text{CCH}=\text{CMe}_2)]$ (**4**) (Scheme 2). The transformation required several days at room temperature but completed in about 6 h in toluene at 363 K. Our monitoring of the transformation by NMR indicated that the isomerization is selective and no intermediate accumulates up to concentrations allowing detection. The solid state structure of **4** (Figure 1, below) indicates that the isomerization process has regenerated the $\kappa P, P, \text{Si}$ pincer ligand, which now coordinates in a *mer* fashion, and converted the 3-methyl-1,2-butadienyl substituent at silicon into a 3-methylbut-2-en-1-ylidyne ligand. The bond distances and angles of the latter match those found in complexes with analogous ligands:¹³ Ru-C(26) 1.717(2) Å, C(26)-C(27) 1.412(3) Å, C(27)-C(28) 1.343(4) Å and C(26)-C(27)-C(28) 124.1(3)°. As proposed in the previous examples, the relatively short C-C single bond could result from the contribution of vinylidene-type canonical forms.¹⁴ Another noteworthy detail in the solid state structure of **4** is the similarity of the two Ru-Cl distances: Ru-Cl(1)

2.5049(6) Å, Ru-Cl(2) 2.5121(6) Å, which evidences that the trans influence of the allenylcarbyne ligand is nearly as high as that of the silyl group.¹⁵ Both Ru-Cl bonds are significantly longer than those in **3**: Ru-Cl(1) 2.3553(7) Å, Ru-Cl(2) 2.4085(7) Å, even though the latter corresponds to a chloride trans to a strongly donor ligand such as the phosphine. The identity of the structure of **4** in solution is supported by key features of the NMR spectra, including ¹³C{¹H} signals that evidence the deshielding of the α - γ carbons of the allenylcarbyne backbone, at δ 288.36 (t, ²*J*_{CP} = 10.9 Hz), 132.20 and 171.49, respectively.

Figure 1. Crystal structures of complexes **3** (above) and **4** (below) at the 50% probability level. The hydrogen atoms are omitted for clarity. For bond distances and angles see the Supporting Information.

The isomerization of **3** into **4** implies a significant rearrangement of the ruthenium coordination sphere but it is triggered by a simple 1,2 hydrogen shift. Given the structure of **3**, the feasibility of such a shift seems rather obvious, as the two carbons involved in the process are within the reach of the metal atom. However, this is not the general case and, in fact, to the best of our knowledge, the tautomerization of an allenyl ligand into an allenylcarbyne has never been reported,^{16,17} not even for allenyl ligands bridging two or more metals. Therefore, this novel transformation can be considered a genuine result of the capability of these pincer complexes to reversibly host reactive fragments in their Ru-Si bond.

EXPERIMENTAL SECTION

General Comments. All manipulations were carried out with exclusion of air by using standard Schlenk techniques or in an argon-filled drybox (MBraun). Solvents were obtained from a solvent purification system (MBraun). Deuterated solvents were dried with appropriate drying agents and degassed with argon prior to use. C, H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. MALDI-TOF MS were obtained in a Bruker Microflex mass spectrometer using DCTB (1,1-dicyano-4-*tert*-butylphenyl-3-methylbutadiene) as the matrix. Infrared spectra were recorded in KBr using a FT-IR Perkin-Elmer Spectrum One spectrometer. NMR spectra were recorded on Bruker Avance 400 or 300 MHz spectrometers. ^1H (400.13 or 300.13 MHz) and ^{13}C (100.6 or 75.5 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to TMS. ^{31}P (162.0 or 121.5 MHz) and ^{29}Si (79.5 or 59.6 MHz) chemical shifts were measured relative to H_3PO_4 (85%) and TMS, respectively. Coupling constants, nJ and $^nJ_{\text{N}}$ ($= ^nJ + ^nJ_{\text{N}}$ for couplings with chemically equivalent but magnetically inequivalent nuclei), are given in hertz. In general, NMR spectral assignments were achieved through ^1H cosy, ^1H nOesy, $^1\text{H}\{^1\text{P}\}$, ^{13}C apt, and $^1\text{H}/^{13}\text{C}$ hsqc experiments. The NMR data are given at room temperature.

Synthesis. The starting complex $[\text{Ru}(\mu\text{-Cl})\{\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**1**) was prepared as previously reported.⁷ All other reagents were commercial and were used as received. The new complexes described below are air-sensitive in solution and solid state.

Preparation of $[\text{Ru}(\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2)\text{Cl}]\{\eta^2\text{-HC}\equiv\text{CC}(\text{OH})\text{Me}_2\}$ (2**).** A solution of **1** (200.0 mg, 0.18 mmol) in toluene (3 mL) was treated with 2-methyl-3-butyn-2-ol (45 μL , 0.46 mmol). After 30 min at room temperature, the resulting greenish yellow solution was concentrated to ca. 0.5 mL and treated with hexane to give a yellow solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 164 mg (70%). Anal. Calcd. for $\text{C}_{30}\text{H}_{47}\text{ClO}_2\text{P}_2\text{RuSi}$: C, 55.41; H, 7.28. Found: C, 55.45; H, 7.25. MS (m/z): 649.8 (M^+). IR (cm^{-1}): 3348 $\nu(\text{OH})$, 1703 $\nu(\text{C}\equiv\text{C})$. ^1H NMR (CD_2Cl_2): δ 0.48 (dd, $^3J_{\text{HP}} = 14.8$, $^3J_{\text{HH}} = 6.9$, 6H, PCHCH_3), 0.86 (dd, $^3J_{\text{HP}} = 15.0$, $^3J_{\text{HH}} = 7.2$, 6H, PCHCH_3), 0.87 (dd, $^3J_{\text{HP}} = 15.0$, $^3J_{\text{HH}} = 6.6$, 6H, PCHCH_3), 0.99 (s, 3H, SiCH_3), 1.34 (dd, $^3J_{\text{HP}} = 12.6$, $^3J_{\text{HH}} = 7.2$, 6H, PCHCH_3), 1.60 (s, 6H, $\text{C}\equiv\text{CCCH}_3$), 2.12, 3.10 (both m, 2H each, PCHCH_3), 6.70 (s, 1H, OH), 7.24, 7.39 (both m, 2H each, CH), 7.50 (dd, $^3J_{\text{HH}} = 7.5$, $^3J_{\text{HP}} = 4.5$, 2H, CH), 7.69 (t, $^3J_{\text{HP}} = 3.0$, 1H, $\text{HC}\equiv\text{C}$), 7.89 (d, $^3J_{\text{HH}} = 7.2$, 2H, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 95.72 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 5.60 (s, SiCH_3), 19.46, 19.67 (both m, PCHCH_3), 20.27 (vt, $^{2,4}N_{\text{CP}} = 4.0$, PCHCH_3), 20.61 (s, PCHCH_3), 26.93, 29.34 (both m, PCHCH_3), 33.25 (s, $\text{C}\equiv\text{CCCH}_3$), 76.08 (s, $\text{C}\equiv\text{CCCH}_3$), 127.21 (brs, $\text{HC}\equiv\text{C}$), 127.75 (vt, $^{3,5}N_{\text{CP}} = 5.3$, CH), 128.91 (vt, $^{3,4}N_{\text{CP}} = 3.1$, CH), 129.84 (s, CH), 132.84 (m, CH), 142.79, 157.40 (both m, C), 172.11 (t, $^2J_{\text{CP}} = 12.7$, $\text{C}\equiv\text{CCCH}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 59.54 (t, $^2J_{\text{SiP}} = 14.3$).

Preparation of $[\text{Ru}(\text{Cl})_2(\kappa\text{P},\text{P-Si}(\text{Me})(1,2\text{-}\eta\text{-CH}=\text{C}=\text{CMe}_2)(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2)]$ (3**).** A solution of **1** (100.0 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was cooled at 243 K and treated with 3-chloro-3-methyl-1-butyne (30 μL , 0.27 mmol). After 30 min, the resulting green solution was warmed up to room temperature (ca. 10 min), concentrated to ca. 0.5 mL and treated with hexane to give a green solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 87 mg (72%). Anal. Calcd. for $\text{C}_{30}\text{H}_{46}\text{Cl}_2\text{P}_2\text{RuSi}$: C, 53.88; H, 6.93. Found: C, 54.23; H, 6.84. MS (m/z): 633.6 ($\text{M}^+ - \text{Cl}$). IR (cm^{-1}): 1761 $\nu(\text{C}=\text{C})$. ^1H NMR (CD_2Cl_2): δ 0.20, 0.76 (both dd, $^3J_{\text{HP}} = 14.0$, $^3J_{\text{HH}} = 7.2$, 3H each, PCHCH_3), 0.89 (s, 3H, SiCH_3), 0.92 (dd, $^3J_{\text{HP}} = 14.3$, $^3J_{\text{HH}} = 7.1$, 3H, PCHCH_3), 1.01 (dd, $^3J_{\text{HP}} = 15.3$, $^3J_{\text{HH}} = 7.2$, 3H, PCHCH_3), 1.27 (dd, $^3J_{\text{HP}} = 11.5$, $^3J_{\text{HH}} = 7.1$, 3H, PCHCH_3), 1.30 (dd, $^3J_{\text{HP}} = 15.4$, $^3J_{\text{HH}} = 7.2$, 3H, PCHCH_3), 1.56 (m, 1H, PCHCH_3), 1.64 (dd, $^3J_{\text{HP}} = 17.0$, $^3J_{\text{HH}} = 6.6$, 3H, PCHCH_3), 1.70 (dd, $^3J_{\text{HP}} = 17.3$, $^3J_{\text{HH}} = 6.7$, 3H, PCHCH_3), 1.80 (m, 1H, $\text{SiCH}=\text{C}=\text{CCH}_3$), 1.92 (d, 3H, $^5J_{\text{HP}} = 2.2$, $\text{SiCH}=\text{C}=\text{CCH}_3$), 1.98 (d, 3H, $^5J_{\text{HP}} = 1.4$, $\text{SiCH}=\text{C}=\text{CCH}_3$), 2.61, 2.74, 3.17 (all m, 1H each, PCHCH_3), 7.30 (m, 2H, CH), 7.37 (m, 3H, CH), 7.47, 7.70, 7.79 (all m, 1H each, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 31.41 (d, $^2J_{\text{PP}} = 19.8$), 96.03 (d, $^2J_{\text{PP}} = 19.8$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -1.81 (s, SiCH_3), 2.21 (d, $^2J_{\text{CP}} =$

11.3, $\text{SiCH}=\text{C}=\text{CCH}_3$), 19.15 (s, PCHCH_3), 19.82 (d, $^2J_{\text{CP}} = 2.8$, PCHCH_3), 20.56 (s, PCHCH_3), 20.85 (d, $^2J_{\text{CP}} = 2.6$, PCHCH_3), 21.18 (d, $^2J_{\text{CP}} = 3.5$, PCHCH_3), 21.21 (d, $^4J_{\text{CP}} = 1.8$, $\text{SiCH}=\text{C}=\text{CCH}_3$), 22.06 (d, $^2J_{\text{CP}} = 3.1$, PCHCH_3), 22.47 (s, PCHCH_3), 22.77 (d, $^2J_{\text{CP}} = 3.6$, PCHCH_3), 26.19 (d, $^1J_{\text{CP}} = 19.9$, PCHCH_3), 27.00 (d, $^4J_{\text{CP}} = 1.4$, $\text{SiCH}=\text{C}=\text{CCH}_3$), 27.42 (d, $^1J_{\text{CP}} = 23.7$, PCHCH_3), 27.88 (d, $^1J_{\text{CP}} = 19.1$, PCHCH_3), 34.72 (d, $^1J_{\text{CP}} = 37.1$, PCHCH_3), 108.66 (s, $\text{SiCH}=\text{C}=\text{CCH}_3$), 128.20 (d, $^3J_{\text{CP}} = 7.2$, CH), 129.61 (d, $^3J_{\text{CP}} = 5.6$, CH), 129.69 (d, $^4J_{\text{CP}} = 2.4$, CH), 129.92 (d, $^3J_{\text{CP}} = 3.9$, CH), 130.32 (d, $^3J_{\text{CP}} = 2.7$, CH), 132.43 (s, CH), 134.27 (d, $^2J_{\text{CP}} = 12.7$, CH), 137.08 (d, $^2J_{\text{CP}} = 13.0$, CH), 137.47 (d, $^1J_{\text{CP}} = 32.3$, C), 140.79 (d, $^2J_{\text{CP}} = 20.2$, C), 141.10 (dd, $^1J_{\text{CP}} = 45.6$, $^3J_{\text{CP}} = 2.9$, C), 146.73 (d, $^2J_{\text{CP}} = 18.5$, C), 174.56 (dd, both $^2J_{\text{CP}} \approx 3.6$, $\text{SiCH}=\text{C}=\text{CCH}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -19.61 (t, $^3J_{\text{SiP}} = 9.2$). The crystals used in the X-ray diffraction experiment were obtained at 253 K from a concentrated solution in CH_2Cl_2 layered with hexane.

Preparation of $[\text{Ru}(\kappa\text{P},\text{P-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2)(\text{Cl})_2(\text{C}\equiv\text{CCH}=\text{CMe}_2)]$ (4**).** A solution of **3** (100.0 mg, 0.15 mmol) in toluene (5 mL) was heated at 363 K for 6 h. Concentration of the resulting brown solution to ca. 0.5 mL and addition of hexane (3 mL) produced a dark orange solid, which was separated by decantation, and dried in vacuo: yield 63 mg (63 %). Anal. Calcd. for $\text{C}_{30}\text{H}_{46}\text{Cl}_2\text{P}_2\text{RuSi}$: C, 53.88; H, 6.93. Found: C, 54.05; H, 6.79. MS (m/z): 633.1 ($\text{M}^+ - \text{Cl}$). ^1H NMR (toluene- d_8): δ 0.70 (s, 3H, SiCH_3), 0.91 (dvt, $^3J_{\text{HH}} = 6.5$, $^{3,5}N_{\text{HP}} = 13.6$, 6H, PCHCH_3), 1.08 (dvt, $^3J_{\text{HH}} = 7.8$, $^{3,5}N_{\text{HP}} = 14.9$, 6H, PCHCH_3), 1.09 (s, 3H, $\equiv\text{CCH}=\text{CCH}_3$), 1.56 (dvt, $^3J_{\text{HH}} = 7.2$, $^{3,5}N_{\text{HP}} = 14.4$, 6H, PCHCH_3), 1.75 (dvt, $^3J_{\text{HH}} = 8.3$, $^{3,5}N_{\text{HP}} = 15.5$, 6H, PCHCH_3), 2.27 (m, 2H, PCHCH_3), 2.38 (s, 3H, $\equiv\text{CCH}=\text{CCH}_3$), 3.57 (m, 2H, PCHCH_3), 4.85 (s, 1H, $\equiv\text{CCH}=\text{CCH}_3$), 7.15 (dd, both $^3J_{\text{HH}} \approx 7.4$, 2H, CH), 7.25 (dd, both $^3J_{\text{HH}} \approx 7.1$, 2H, CH), 7.36 (m, 2H, CH), 8.06 (d, $^3J_{\text{HH}} = 7.2$, 2H, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8): δ 67.15 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): δ 9.76 (s, SiCH_3), 19.54, 20.17, 21.02, 21.41 (all s, PCHCH_3), 24.53, 25.82 (both s, $\equiv\text{CCH}=\text{CCH}_3$), 27.72 (vt, $^{1,3}N_{\text{CP}} = 22.2$, PCHCH_3), 29.69 (vt, $^{1,3}N_{\text{CP}} = 20.8$, PCHCH_3), 127.46 (vt, $^{3,5}N_{\text{CP}} = 6.8$, CH), 129.35 (s, CH), 131.79 (vt, $^{3,4}N_{\text{CP}} = 3.0$, CH), 132.20 (s, $\equiv\text{CCH}=\text{CCH}_3$), 133.47 (vt, $^{2,4}N_{\text{CP}} = 18.4$, CH), 139.99 (vt, $^{1,3}N_{\text{CP}} = 48.5$, C), 158.05 (vt, $^{2,3}N_{\text{CP}} = 34.6$, C), 171.49 (s, $\equiv\text{CCH}=\text{CCH}_3$), 288.36 (t, $^2J_{\text{CP}} = 10.9$, $\equiv\text{CCH}=\text{CCH}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (toluene- d_8): δ 41.61 (t, $^2J_{\text{SiP}} = 5.8$). The crystals used in the X-ray diffraction experiment were obtained from a CH_2Cl_2 solution stored at 253 K.

X-ray Crystallography. X-ray data were collected at 100.0(2) K on Bruker SMART APEX area detector diffractometer equipped with a normal focus, 2.4 kW, sealed tube source (molybdenum radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. In both cases, single crystals were mounted on a fiber and covered with protective perfluoropolyether. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 20 s, covering 0.3° in ω . Data were corrected for absorption by using a multi-scan method applied with the SADABS program.¹⁸ The structures were solved by the Patterson method and refined by full-matrix least squares on F^2 using the Bruker SHELXTL program package,¹⁹ including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. Weighted R factors (R_w) and goodness of fit (S) are based on F^2 , and conventional R factors are based on F . Hydrogen atoms were included in calculated positions and refined riding on the corresponding carbon atoms, or in observed positions and refined freely. For both structures the highest electronic residuals were observed in close proximity of the Ru center and make no chemical sense.

Data for 3. $\text{C}_{30}\text{H}_{46}\text{Cl}_2\text{P}_2\text{SiRu} \cdot \text{CH}_2\text{Cl}_2$, $M = 753.59$; green irregular block, $0.14 \times 0.08 \times 0.08$ mm³; orthorhombic, $P2(1)2(1)2(1)$; $a = 13.6093(10)$ Å, $b = 15.4875(11)$ Å, $c = 16.3073(12)$ Å; $Z = 4$; $V = 3437.2(4)$ Å³; $D_c = 1.456$ g·cm⁻³; $\mu = 0.916$ mm⁻¹, minimum and maximum transmission factors 0.736 and 0.934; $2\theta_{\text{max}} = 57.10$; 41086 reflections collected, 8201 unique [$R(\text{int}) = 0.0563$]; number of data/restraints/parameters 8201/0/367; final GoF 0.912, $R1 = 0.0301$ [6755 reflections $I > 2\sigma(I)$], $wR2 = 0.0515$ for all data; largest peak and hole 0.595 and -0.734 e⁻Å⁻³. Flack parameter resulted in $-0.001(1)$, which indicates that the absolute structure is correct.

Data for **4**. $C_{30}H_{46}Cl_2P_2SiRu_2(CH_2Cl_2)_2$, $M = 838.52$; orange irregular block, $0.08 \times 0.06 \times 0.04 \text{ mm}^3$; triclinic, $P\bar{1}$; $a = 9.8915(7) \text{ \AA}$, $b = 11.2760(8) \text{ \AA}$, $c = 18.3524(13) \text{ \AA}$; $\alpha = 84.3720(10)$, $\beta = 84.2390(10)$, $\gamma = 68.6740(10)$; $Z = 2$; $V = 1893.0(2) \text{ \AA}^3$; $D_c = 1.471 \text{ g cm}^{-3}$; $\mu = 0.976 \text{ mm}^{-1}$, minimum and maximum transmission factors 0.817 and 0.955; $2\theta_{\text{max}} = 59.18$; 20015 reflections collected, 9611 unique [$R(\text{int}) = 0.0295$]; number of data/restraints/parameters 9611/0/394; final GoF 0.942, $R1 = 0.0334$ [7839 reflections $I > 2\sigma(I)$], $wR2 = 0.0845$ for all data; largest peak and hole 1.593 and $-0.884 \text{ e}^{-\text{\AA}^{-3}}$.

ASSOCIATED CONTENT

Supporting Information

Figures and CIF files giving the NMR spectra of compounds **2-4** and crystal data for **3** and **4**. 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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