Arene and Hydride Complexes of Ruthenium with *fac* PSiP Pincer Ligands

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Dedicated to Professor F. Ekkehardt Hahn on the Occasion of His 60th Birthday

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Abstract. Several derivatives of the dinuclear complex $[\text{Ru}(\mu\text{-Cl})\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**1**) are described. The mononuclear cationic arene complex $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}(\eta^6\text{-C}_6\text{H}_6)](\text{CF}_3\text{SO}_3)$ (**5**), the phosphane adduct $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}\text{Cl}(\text{PPh}_3)]$ (**2**), and the hydride-bridged dinuclear derivatives $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-H})\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**6**) and $[\text{Ru}_2(\mu\text{-H})\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**7**) retain the *fac* coordination mode of the $\kappa P,P,\text{Si}$

ligand present in the precursor complex. In contrast, the neutral and cationic acetonitrile derivatives $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}\text{Cl}(\text{NCMe})_2]$ (**3**) and $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}(\text{NCMe})_3](\text{CF}_3\text{SO}_3)$ (**4**), respectively, show the PSiP pincer coordinated in the more usual *mer* fashion. Crystal structures determined by X-ray diffraction are shown for complexes **5**, **6** and **7**. The factors that influence the choice of coordination mode for the PSiP ligand are discussed.

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Introduction

Pincer ligands have become important tools in coordination chemistry and homogeneous catalysis.^[1] Initially they were just regarded as a class of particularly stabilizing tridentate ligands, but the development of their chemistry is showing that they can also provide to their complexes stereoelectronic diversity and exceptional noninnocent functional contributions.^[1-3] In particular, PSiP pincers have emerged capable of dictating the coordination geometry of unsaturated complexes via the *trans* influence of the silyl group,^[4] and have proved able to assist organometallic transformations through reversible formations of Si-C bonds.^[5] The versatility of these PSiP ligands also spans their most basic coordination properties, since the meridional (*mer*) coordination mode typical of pincer ligands in octahedral environments often turn into facial (*fac*) as a result of minor changes.^[6] Aimed to discuss the reasons behind this choice of coordination modes, this work presents several ruthenium complexes that contain the PSiP ligand $[\text{Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2]$ coordinated as *fac* $\kappa P,P,\text{Si}$. In spite of the actual structures, the examples suggest that the *mer* coordination of this pincer is indeed the more favorable in the absence of constraints.

Results and Discussion

The dimer $[\text{Ru}(\mu\text{-Cl})\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}]_2$ (**1**),^[5a] just as its analogue with cyclohexyl instead isopropyl

groups,^[7] has proved to be an excellent starting material in the chemistry of Ru(PSiP) complexes and can indeed initiate the set of reactions shown in Scheme 1. Nevertheless, the compounds in this scheme are also accessible from the more common and commercially available $[\text{RuCl}_2(\text{PPh}_3)_3]$. The reaction of the latter with the PSiP ligand precursor $\text{HSi}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2$ gave the complex $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}\text{Cl}(\text{PPh}_3)]$ (**2**), which remained five-coordinate despite the triphenylphosphane excess. Complex **2** also has a reported analogue characterized by X-ray diffraction, in this case with a phenyl-substituted PSiP ligand.^[8] In solution at room temperature, the NMR spectra of **2** (so as those of its analogue) only showed broad signals that suggest a dynamic structure. Below 200 K, the spectra indicated the presence of a single compound, whose main structural features could be easily inferred from the $^{31}\text{P}\{^1\text{H}\}$ signals. They consist of three doublets of doublets at $\delta = 39.66$, 65.34 and 103.66 ppm, respectively. The former corresponds to the PPh_3 ligand and shows two very different $J(\text{P,P})$ coupling constants of 268.6 and 23.8 Hz, while the mutual coupling between the phosphorous of the pincer is 21.2 Hz. Obviously, the chloride ligand could not be located by these NMR methods, so that its proposed coordination, halfway between the two positions still available in the octahedron, is that found in the aforementioned analogue. Considering that coordination *trans* to phosphorous should be favored versus that *trans* to the more strongly donor silyl group, this uncommon coordination position of the chloride could tentatively be attributed to the steric congestion in the plane shared by the three phosphane fragments.

The proposed steric congestion in **2** may also explain the ease with which the PPh_3 ligand is substituted by weak ligands such as acetonitrile. The treatment of **2** with this solvent readily gave the six-coordinate complex $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}\text{Cl}(\text{NCMe})_2]$ (**3**). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of this compound clearly evidenced the *mer* coordination of the PSiP ligand by showing virtual triplet signals for the hydrogens and carbons coupled to both magnetically inequivalent and strongly

coupled, mutually *trans* phosphorous atoms. The very occurrence of this substitution reaction and the parallel change of the PSiP coordination mode strongly suggest that a *mer* arrangement is preferred when there is no need to accommodate bulky co-ligands. In this context, is worth mentioning that in the previously reported complex $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4-2\text{-PiPr}_2)_2\}\text{Cl}(\text{CO})]$, an analogue of **2** with CO instead of PPh_3 , the PSiP ligand coordinates in the *mer* fashion.^[5a]

Scheme 1. Synthesis of complexes **2**–**5**.

The ^1H NMR spectra of complex **3** at room temperature featured sharp signals for all hydrogens, including those of the two inequivalent acetonitriles, but the signal in the $^{31}\text{P}\{^1\text{H}\}$ spectrum was occasionally slightly broadened. This broad singlet was found to decoalesce at low temperature into two: a major one corresponding to **3** and another due to the tris-acetonitrile cation $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4-2\text{-PiPr}_2)_2\}(\text{NCMe})_3]^+$ (**4** in Scheme 1), whose integral depended on the amount of free acetonitrile present in the sample. First of all, this observation indicates that the chloride is the most labile ligand in the coordination sphere of **3** and therefore supports the structure proposed for the complex, which features mutually *trans* (non-labile)^[9] acetonitriles and the chloride *trans* to the *trans*-labilizing silyl group. The tris-acetonitrile cationic complex **4** was independently prepared with triflate as counterion by treatment of **3** with the corresponding silver salt in the presence of acetonitrile. Its NMR data confirm the identity of the low temperature companion of **3**, also indicating that the replacement of chloride by a third acetonitrile does not alter the PSiP coordination mode.

When the reaction with silver triflate was started from **2** in the presence of benzene, the removal of chloride together

with the easy phosphane substitution led to the formation of the benzene complex $[\text{Ru}\{\kappa P,P,\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4-2\text{-PiPr}_2)_2\}(\eta^6\text{-C}_6\text{H}_6)](\text{CF}_3\text{SO}_3)$ (**5**). The X-ray structure in Figure 1 confirms that the PSiP ligand adopts the *fac* coordination mode required to accomplish the η^6 coordination of the arene. As expected, **5** formed **4** after treatment with acetonitrile, again showing that when constraints disappear the *mer* coordination of the PSiP is favored.

Figure 1. Crystal structure of the cation of complex **5** at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å: Ru(1)–P(1) 2.334(6), Ru(1)–P(2) 2.356(4), Ru(1)–Si(1) 2.357(4), Ru(1)–C 2.247(16), 2.278(16), 2.308(18), 2.351(17), 2.260(17), 2.270(16). Selected bond angles /°: P(1)–Ru(1)–P(2) 95.49(17), P(1)–Ru(1)–Si(1) 81.61(17). Only the cation of one of the two crystallographically independent cations is shown and described. For more details see the Supporting Information.

The structure of **5** reveals a conformation of the PSiP ligand that is far from symmetrical. While this is a common feature in the solid state for this type of ligands in the *fac* mode, the NMR data of **5** indicate that, exceptionally, such asymmetric coordination persists in solution. Again, the NMR spectra of the complex were found to show broad, featureless, non-informative signals at room temperature. The evolution of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at low temperature, however, clearly indicated the presence of two compounds, in approximately 4:1 molar ratio, that transform into each other fast in the NMR time scale. Both compounds lack of symmetry plane, each one showing spectra that consist of two doublets with a mutual $J(\text{P},\text{P})$ coupling constant of 33.0 Hz for the major compound and 31.2 Hz for the minor. Accordingly, both asymmetric compounds should contain *fac* PSiP ligands. Although the experimental data do not allow a more precise identification of the two exchanging compounds, they are most probably conformers, since it is likely that each non-symmetric conformation of the PSiP forces a different relative position of the arene ligand in the coordination sphere. In fact, the low temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra also showed decoalescence of the room temperature singlets corresponding to the benzene ligand into two, of relative intensity 4:1, that should correspond to different, fast rotating, arene ligands. On the contrary, the ^{19}F NMR signal corresponding to the triflate remained unique and sharp at any temperature, thus discarding any relevant role of the anion coordination in the observed behavior. In any case, the experimental $^{31}\text{P}\{^1\text{H}\}$ NMR data did permit the estimation of the activation parameters for the exchange (see supporting information for more details) as $\Delta H^\ddagger = 9.6 \pm 0.2$

Kcal mol⁻¹ and $\Delta S^\ddagger = 0.2 \pm 0.7$ cal K⁻¹ mol⁻¹, in agreement with a facile intramolecular process.

The dimer **1** was also found suitable to prepare hydride derivatives. Its treatment with NaH in THF led to the sequential formation of two new compounds: the mixed-bridged complex [Ru₂(μ-Cl)(μ-H){κP,P,Si-Si(Me)(C₆H₄-2-PiPr₂)₂}]₂ (**6**) and the doubly hydride-bridged derivative [Ru₂(μ-H){κP,P,Si-Si(Me)(C₆H₄-2-PiPr₂)₂}]₂ (**7**) (Scheme 2). Due to the sequential nature of the reaction, the poor stability of the final product **7**, and the presence of small amounts of side products, none of these hydrides could be isolated as analytically pure solid, although we managed to get single crystals of both complexes to accomplish their X-ray characterization (Figure 2). In addition, the compounds were characterized by solution NMR from isolated solids in which they were the very major components.

Scheme 2. Synthesis of the dinuclear hydride complexes **6** and **7**.

The going of the sequence of Scheme 2 involves small changes in the square-pyramidal coordination spheres of the individual ruthenium centers (Table 1) but a significant progressive shortening of the intermetallic separation to keep the bridging hydrides within bonding distances. The Ru...Ru distance found in **1**, 3.7710(4) Å,^[5a] changes to 2.9834(2) Å after the replacement of the first chloride, and shortens even further to 2.6774(4) Å in complex **7**. As a consequence, the arrangement of the mononuclear fragments within the dimer changes, since the eclipsed configuration of the silyl groups observed in **1** (both upwards in Scheme 2) seems no longer possible for **2** and **3** due to steric congestion. The NMR spectra of the mixed-bridged complex **6** in C₆D₆ displayed ¹H hydride and ³¹P{¹H} signals that confirmed the integrity of the dimeric structure in solution (Figure 3), but the same conclusion was not that evident from the spectra of **7**. The hydride ¹H NMR signals of **7** in [D₈]toluene or [D₈]tetrahydrofuran, which once again were broad and featureless at most temperatures, only became relatively sharp on heating, then showing multiple *J*(H,P) coupling constants. Even though the NMR signal broadenings could stem from mononuclear fragments coexisting in equilibrium, these multiple *J*(H,P) couplings confirm that the complex exists as dinuclear also in solution. This proves that the

reduced steric demand of the pincer in the *fac* mode allows the approaching of [Ru(PSiP)] fragments to significantly short distances.

Figure 2. Crystal structures of complex **6** (above) and **7** (below) at the 50% probability level. The hydrogen atoms, except the hydrides, are omitted for clarity. For bond distances and angles, see Table 1.

Figure 3. ³¹P{¹H} (right) and hydride ¹H (left) NMR signals of complexes **6** (above, C₆D₆ at room temperature) and **7** (below, [D₈]thf at 313 K).

Table 1. Selected bond lengths /Å and bond angles /° of **6** and **7**.

	6	7
Ru(1)–P(1)	2.3061(4)	2.3008(11)
Ru(1)–P(2)	2.2827(4)	2.3070(12)
Ru(2)–P(3)	2.3073(4)	2.3075(12)
Ru(2)–P(4)	2.2983(4)	2.2925(11)
Ru(1)–Cl	2.3592(4)	
Ru(2)–Cl	2.3731(4)	
Ru(1)–Si(1)	2.2515(5)	2.2476(11)
Ru(2)–Si(2)	2.2569(5)	2.2496(11)
Ru(1)–Cl–Ru(2)	78.164(14)	
P(1)–Ru(1)–P(2)	102.037(16)	99.97(4)
P(3)–Ru(2)–P(4)	101.612(15)	99.73(4)
P(1)–Ru(1)–Cl	94.544(15)	
P(2)–Ru(1)–Cl	162.616(16)	
P(3)–Ru(2)–Cl	93.457(15)	
P(4)–Ru(2)–Cl	164.693(16)	
Cl–Ru(1)–Si(1)	103.702(18)	
Cl–Ru(2)–Si(2)	101.559(17)	

Conclusions

The compounds and reactions shown in the previous lines illustrate that the $\kappa P,P,Si$ ligand $[Si(Me)(C_6H_4-2-PiPr_2)_2]$ can adapt its coordination mode to the constraints imposed by the other ligands in the coordination sphere of their complexes. The *fac* mode, uncommon for pincer ligands, is obviously the choice when another *fac* ligand needs to be accommodated, as happens in the η^6 -benzene complex **5**, but it is also the preferred option when bulky ligands are present, as in the PPh_3 complex **2**, or when dimerization can relieve the coordinative unsaturation of the complexes, as occurs for **1**, **6** and **7**. In the absence of constraints, the *mer* coordination mode of the ligand seems to be favored.

Experimental Section

General experimental methods: 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 and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Matrix-assisted laser desorption ionization mass spectra were recorded with 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. ^{19}F (376.5 MHz), ^{31}P (162.0 or 121.5 MHz) and ^{29}Si (59.6 MHz) chemical shifts were measured relative to $CFCl_3$, H_3PO_4 (85%) and TMS, respectively. Coupling constants, ^nJ and $^{n,m}N$ ($= ^nJ + ^mJ'$ for couplings with chemically equivalent but magnetically inequivalent nuclei), are given in hertz. In general, NMR spectral assignments were achieved through ^1H cosy, $^1H\{^{31}P\}$, ^{13}C apt, $^1H/^{13}C$ hsqc and $^1H/^{13}C$ hmhc experiments. Unless otherwise indicated, the NMR data are given at room temperature.

Synthesis and characterization: The starting complexes $RuCl_2(PPh_3)_3$,^[10] $[Ru(\mu-Cl)\{\kappa P,P,Si-Si(Me)(C_6H_4-2-PiPr_2)_2\}]_2$ (**1**)^[5a] and the diphosphane $HSi(Me)(C_6H_4-2-PiPr_2)_2$,^[6a] were prepared as previously reported. All other reagents were commercially available and used as received. The new complexes described below are air-sensitive in solution and solid state.

Preparation of $[Ru\{\kappa P,P,Si-Si(Me)(C_6H_4-2-PiPr_2)_2\}Cl(PPh_3)]$ (2**).** $[RuCl_2(PPh_3)_3]$ (1.774 g, 1.85 mmol) was added to a solution of $HSi(Me)(C_6H_4-2-PiPr_2)_2$ (0.797 g, 1.85 mmol) in toluene (45 mL) and treated with 6 mL of neat NEt_3 . The red-brownish heterogeneous mixture was refluxed for 15 h, cooled to room temperature, and concentrated to 10 mL to evaporate the NEt_3 excess. After filtering to remove the solid $NEt_3 \cdot HCl$, the solution was further evaporated under reduced pressure to ca. 0.5 mL and treated with hexane (3 mL) to give an orange solid. The solid was separated by decantation, washed with hexane and dried in vacuo. Yield 797 mg (52 %). $C_{43}H_{54}ClP_3SiRu$ (828.43): calcd. C 62.34, H 6.57 %; found C 62.42, H 6.85 %. **^1H NMR** (CD_2Cl_2 , 183 K): δ = –1.01 (dd, $^3J_{H,P}$ = 14.4, $^3J_{H,H}$ = 5.7, 3H, $PCHCH_3$), 0.22 (s, 3H, $SiCH_3$), 0.80 (m, 6H, $PCHCH_3$), 0.89 (dd, $^3J_{H,P}$ = 10.0, $^3J_{H,H}$ = 6.1, 3H, $PCHCH_3$), 0.99 (dd, $^3J_{H,P}$ = 8.3, $^3J_{H,H}$ = 6.2, 3H, $PCHCH_3$), 1.27 (dd, $^3J_{H,P}$ = 14.4, $^3J_{H,H}$ = 6.5, 3H, $PCHCH_3$), 1.63 (dd, $^3J_{H,P}$ = 13.3, $^3J_{H,H}$ = 6.2, 3H, $PCHCH_3$), 1.87 (dd, $^3J_{H,P}$ = 14.5, $^3J_{H,H}$ = 6.5, 3H, $PCHCH_3$), 2.15 (m, 1H, $PCHCH_3$), 2.96 (m, 2H, $PCHCH_3$), 3.26 (m, 1H, $PCHCH_3$), 6.34 (brdd, both $^3J_{H,H} \approx 7.4$, 2H, CH), 6.57 (brdd, both $^3J_{H,H} \approx 6.7$, 2H, CH), 6.77 (brdd, both $^3J_{H,H} \approx 5.6$, 2H, CH), 6.85 (brdd, both $^3J_{H,H} \approx 6.7$, 2H, CH), 6.90 (dd, both $^3J_{H,H} \approx 7.3$, 2H, CH), 7.14–7.24 (m, 5H, CH), 7.27–7.40 (m, 7H, CH), 7.60 (br, 1H, CH), 7.67 (d, $^3J_{H,H} \approx 7.1$, 1H, CH), 7.77 (brm, 1H, CH), 7.83 (d, $^3J_{H,H} \approx 7.1$, 1H, CH). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2 , 183 K): δ = 39.66 (dd, $^2J_{P,P}$ = 268.6, 23.8, 1P, PPh_3), 65.34 (dd, $^2J_{P,P}$ = 268.6, 21.2, 1P, $PCHCH_3$), 103.20 (dd, $^2J_{P,P}$ = 23.8, 21.2, 1P, $PCHCH_3$). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2 , 183 K): δ = 2.20 (s, $SiCH_3$), 17.21 (d, $^2J_{C,P}$ = 5.4, $PCHCH_3$), 18.04 (s, $PCHCH_3$), 19.20 (d, $^2J_{C,P}$ = 1.5, $PCHCH_3$), 20.19 (s, $PCHCH_3$), 20.36 (d, $^2J_{C,P}$ = 7.5, $PCHCH_3$), 20.98 (d, $^2J_{C,P}$ = 5.4, $PCHCH_3$), 21.59 (d, $^2J_{C,P}$ = 2.3, $PCHCH_3$), 24.49 (dd, $^1J_{C,P}$ = 12.7, $^3J_{C,P}$ = 2.9, $PCHCH_3$), 26.62 (d, $^1J_{C,P}$ = 25.9, $PCHCH_3$), 32.11 (dd, $^1J_{C,P}$ = 23.4, $^3J_{C,P}$ = 2.9, $PCHCH_3$), 37.58 (dd, $^1J_{C,P}$ = 24.0, $^3J_{C,P}$ = 15.0, $PCHCH_3$), 125.66 (d, $J_{C,P}$ = 4.5, CH), 125.97, 127.29 (both brs, CH), 127.66 (s, CH), 127.81 (d, $J_{C,P}$ = 11.8, CH), 128.43 (d, $J_{C,P}$ = 12.4, CH), 128.56 (s, CH), 128.83 (d, $J_{C,P}$ = 5.4, CH), 129.14 (d, $J_{C,P}$ = 12.5, CH), 130.73 (d, $^3J_{C,P}$ = 20.1, CH), 130.97 (d, $^3J_{C,P}$ = 23.4, CH), 131.71 (d, $^1J_{C,P}$ = 33.5, C), 133.69 (d, $J_{C,P}$ = 8.7, CH), 133.95 (brd, $J_{C,P}$ = 9.2, CH), 134.38 (dd, $^1J_{C,P}$ = 29.8, 2.0, C), 135.21 (brd, $^1J_{C,P}$ = 38.4, C), 136.36 (d, $J_{C,P}$ = 9.3, CH), 139.18 (d, $^1J_{C,P}$ = 38.2, C), 143.34 (d, $^1J_{C,P}$ = 44.2, C), 157.36 (d, $^2J_{C,P}$ = 46.2, C), 160.26 (d, $^2J_{C,P}$ = 47.2, C). **$^{29}Si\{^1H\}$ NMR** (CD_2Cl_2 , 183 K): δ = 62.08 (ddd, $^2J_{Si,P}$ = 27.1, two $^2J_{Si,P} \approx 13.4$).

Preparation of $[Ru\{\kappa P,P,Si-Si(Me)(C_6H_4-2-PiPr_2)_2\}Cl(NCMe)_2]$ (3**).** A solution **2** (200.0 mg, 0.24 mmol) in acetonitrile (3 mL) was stirred for 5 min at room temperature and then concentrated to 0.5 mL under reduced pressure. Addition of hexane (3 mL) gave a yellow solid, which was separated by decantation, washed with hexane and dried in vacuo. Yield 101 mg (65 %). $C_{29}H_{45}ClN_2P_2SiRu$ (648.25): calcd. C 53.73, H 7.00, N 4.32 %; found: C 53.66, H 6.65, N 4.28 %. **IR:** ν = 2260 $\nu(C\equiv N)$ cm^{-1} . **^1H NMR** (CD_2Cl_2): δ = 0.44 (s, 3H, $SiCH_3$), 0.94 (t, $^5J_{H,P}$ = 1.3, 3H, $NCCH_3$), 0.99 (dvt, $^3J_{H,H}$ = 6.9, $^{3,5}N_{C,P}$ = 14.0, 6H, $PCHCH_3$), 1.23 (dvt, $^3J_{H,H}$ = 5.8, $^{3,5}N_{C,P}$ = 11.1, 6H, $PCHCH_3$), 1.26 (dvt, $^3J_{H,H}$ = 6.7, $^{3,5}N_{C,P}$ = 13.6, 6H, $PCHCH_3$), 1.67 (dvt, $^3J_{H,H}$ = 7.5, $^{3,5}N_{C,P}$ = 14.5, 6H, $PCHCH_3$), 2.23 (t, $^5J_{H,P}$ = 1.3, 3H, $NCCH_3$), 2.37, 3.15 (both m, 2H each, $PCHCH_3$), 7.25 (ddd, two $^3J_{H,H} \approx 7.4$, $^4J_{H,H}$ = 1.1,

2H, CH), 7.33 (ddd, two $^3J_{\text{H,H}} \approx 7.2$, $^4J_{\text{H,H}} = 1.1$, 2H, CH), 7.60 (m, 2H, CH), 8.14 (dd, $^3J_{\text{H,H}} \approx 6.9$, $^4J_{\text{H,H}} = 1.1$, 2H, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 59.63$ (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 233 K): $\delta = 3.25$, 5.24 (both s, NCCH_3), 6.22 (s, SiCH_3), 17.48, 17.55, 19.03, 20.08 (all s, PCHCH_3), 25.72 (vt, $^{13}\text{N}_{\text{C,P}} = 19.0$, PCHCH_3), 26.15 (vt, $^{13}\text{N}_{\text{C,P}} = 17.3$, PCHCH_3), 121.94, 123.08 (both s, NCCH_3), 126.30 (vt, $^{4,5}\text{N}_{\text{C,P}} = 4.9$, CH), 127.69, 130.32 (both s, CH), 132.28 (vt, $^{3,4}\text{N}_{\text{C,P}} = 17.8$, CH), 141.45 (vt, $^{13}\text{N}_{\text{C,P}} = 37.9$, C), 161.11 (vt, $^{2,3}\text{N}_{\text{C,P}} = 43.0$, C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 233 K): $\delta = 55.85$ (t, $^2J_{\text{Si,P}} = 11.2$).

Preparation of $[\text{Ru}\{\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}(\text{NCMe})_3](\text{CF}_3\text{SO}_3)$ (4). A solution of **5** (150.0 mg, 0.20 mmol) in acetonitrile (5 mL) was refluxed for 12 h. The resulting solution was filtered through Celite and concentrated to ca. 0.5 mL under reduced pressure. Addition of hexane (3 mL) produced a pale yellow solid, which was separated by decantation, washed with hexane, and dried in vacuo. Yield 110.5 mg (70 %). $\text{C}_{32}\text{H}_{48}\text{F}_3\text{N}_3\text{O}_3\text{P}_2\text{SSiRu}$ (802.91): calcd. C 47.87, H 6.03, 5.23 N %; found: C 47.42, H 5.93, N 4.91 %. IR: $\nu = 2266$ $\text{v}(\text{C}\equiv\text{N})$ cm^{-1} . ^1H NMR (CD_2Cl_2): $\delta = 0.48$ (s, 3H, SiCH_3), 0.93 (t, $^5J_{\text{H,H}} = 1.2$, 3H, NCCH_3), 0.94 (dvt, $^3J_{\text{H,H}} = 7.8$, $^{3,5}\text{N}_{\text{C,P}} = 15.0$, 6H, PCHCH_3), 1.06 (dvt, $^3J_{\text{H,H}} = 7.2$, $^{3,5}\text{N}_{\text{C,P}} = 14.1$, 6H, PCHCH_3), 1.23 (dvt, $^3J_{\text{H,H}} = 7.7$, $^{3,5}\text{N}_{\text{C,P}} = 11.7$, 6H, PCHCH_3), 1.49 (dvt, $^3J_{\text{H,H}} = 7.5$, $^{3,5}\text{N}_{\text{C,P}} = 14.4$, 6H, PCHCH_3), 2.29 (t, $^5J_{\text{H,H}} = 1.2$, 3H, NCCH_3), 2.31 (m, 2H, PCHCH_3), 2.39 (s, 3H, NCCH_3), 3.08 (m, 2H, PCHCH_3), 7.32, 7.39 (both ddd, two $^3J_{\text{H,H}} \approx 7.4$, $^4J_{\text{H,H}} = 1.2$, 2H each, CH), 7.57 (m, 2H, CH), 8.15 (dd, $^3J_{\text{H,H}} \approx 7.4$, $^4J_{\text{H,H}} = 0.9$, 2H, CH). ^{19}F NMR (CD_2Cl_2): $\delta = -78.9$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 64.01$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 3.19$, 4.10, 4.87 (all s, NCCH_3), 6.09 (s, SiCH_3), 17.90 (vt, $^{2,4}\text{N}_{\text{C,P}} = 2.3$, PCHCH_3), 18.04 (vt, $^{2,4}\text{N}_{\text{C,P}} = 6.1$, PCHCH_3), 19.87 (vt, $^{2,4}\text{N}_{\text{C,P}} = 4.0$, PCHCH_3), 20.29 (s, PCHCH_3), 25.47 (vt, $^{13}\text{N}_{\text{C,P}} = 18.1$, PCHCH_3), 26.82 (vt, $^{13}\text{N}_{\text{C,P}} = 21.1$, PCHCH_3), 121.48 (q, $^1J_{\text{CF}} = 321.0$, CF_3SO_3), 124.74 (s, NCCH_3), 125.03 (br, NCCH_3), 125.49 (s, NCCH_3), 127.43 (vt, $^{4,5}\text{N}_{\text{C,P}} = 4.9$, CH), 129.09 (vt, $^{3,5}\text{N}_{\text{C,P}} = 2.0$, CH), 130.88 (vt, $^{2,4}\text{N}_{\text{C,P}} = 3.5$, CH), 133.31 (vt, $^{3,4}\text{N}_{\text{C,P}} = 18.8$, CH), 140.22 (vt, $^{13}\text{N}_{\text{C,P}} = 41.4$, C), 160.17 (vt, $^{2,3}\text{N}_{\text{C,P}} = 43.6$, C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 54.67$ (t, $^2J_{\text{Si,P}} = 10.8$).

Preparation of $[\text{Ru}\{\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}(\eta^6\text{-C}_6\text{H}_6)](\text{CF}_3\text{SO}_3)$ (5). Method a: A red solution of **2** (150.0 mg, 0.18 mmol) in benzene (5 mL) was added to a solution of silver triflate (46.5 mg, 0.18 mmol) in acetone (5 mL), and stirred for 4 h in the dark at room temperature. The resulting suspension was filtered through Celite to remove the insoluble silver chloride and concentrated to ca. 0.5 mL. Addition of hexane (3 mL) produced a pale yellow solid, which was separated by decantation, washed with hexane, and dried in vacuo. Yield 61 mg (67 %). Method b: The same procedure starting from **1** (300.0 mg, 0.26 mmol) and silver triflate (136.2 mg, 0.53 mmol). Yield 310 mg (77%). $\text{C}_{32}\text{H}_{45}\text{F}_3\text{O}_3\text{P}_2\text{SSiRu}$ (757.86): calcd. C 50.71, H 5.99 %; found: C 50.46, H 6.01 %. MS: $m/z = 609.2$ (M^+). The NMR spectra obtained from the isolated solid in CD_2Cl_2 at 183 K indicated a mixture of two products in relative proportion 4:1. Data for the *major* product: ^1H NMR (CD_2Cl_2 , 183 K): $\delta = -0.79$, 0.41, 0.84 (all br, 3H each, PCHCH_3), 1.04 (s, 3H, SiCH_3), 1.10 (br, 6H, PCHCH_3), 1.38 (br, 9H, PCHCH_3), 1.68, 2.13, 2.54, 2.90 (all br, 1H each, PCHCH_3), 5.99 (s, 6H, C_6H_6), 7.10 (br dd, both $^3J_{\text{H,H}} \approx 5.9$, 1H, CH), 7.22 (br, 3H, CH), 7.38 (br dd, both $^3J_{\text{H,H}} \approx 6.4$, 1H, CH), 7.46, 7.56 (both br, 1H each, CH), 7.82 (br d, $^3J_{\text{H,H}} \approx 6.3$, 1H, CH). ^{19}F NMR (CD_2Cl_2): $\delta = -78.8$ (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 73.66$, 91.30 (both d, $^2J_{\text{P,P}} = 33.0$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 2.02$ (s, SiCH_3), 16.72, 18.29 (both br, PCHCH_3), 18.84 (s, PCHCH_3), 19.35 (br, PCHCH_3), 19.55 (br d,

$^1J_{\text{C,P}} = 22.9$, PCHCH_3), 20.00, 20.58 (both s, PCHCH_3), 21.92 (br, PCHCH_3), 22.94 (d, $^1J_{\text{C,P}} = 20.8$, PCHCH_3), 28.52 (d, $^1J_{\text{C,P}} = 18.6$, PCHCH_3), 30.81 (brd, $^1J_{\text{C,P}} = 31.1$, PCHCH_3), 91.64 (s, C_6H_6), 119.75 (q, $^1J_{\text{C,F}} = 319.9$, CF_3SO_3), 126.92 (br, CH), 127.26 (brd, $J_{\text{C,P}} = 4.6$, CH), 129.01 (s, CH), 129.39 (br, CH), 129.57 (s, CH), 130.73 (d, $^3J_{\text{C,P}} = 17.6$, CH), 131.25 (br, CH), 132.33 (d, $^3J_{\text{C,P}} = 17.9$, CH), 137.59 (d, $^1J_{\text{C,P}} = 45.6$, C), 145.21 (d, $^1J_{\text{C,P}} = 50.9$, C), 153.09 (d, $^2J_{\text{C,P}} = 41.1$, C), 154.39 (d, $^2J_{\text{C,P}} = 42.3$, C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 57.75$ (dd, both $^2J_{\text{Si,P}} \approx 16.0$). Partial data for the *minor* product: ^1H NMR (CD_2Cl_2 , 183 K): $\delta = -0.29$, (br, 3H, PCHCH_3), 1.09 (s, 3H, SiCH_3), 6.14 (s, 6H, C_6H_6). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 74.30$ (d, $^2J_{\text{P,P}} = 31.2$), 88.64 (d, $^2J_{\text{P,P}} = 31.2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 3.51$ (s, SiCH_3), 21.03 (br, PCHCH_3), 90.87 (br s, C_6H_6). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): $\delta = 50.00$ (dd, both $^2J_{\text{Si,P}} \approx 4.6$). The crystals used in the X-ray diffraction experiment were obtained from a benzene solution at room temperature.

$[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-H})\{\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}_2]$ (6). A solution of **1** (125.0 mg, 0.11 mmol) in THF (5 mL) was treated with sodium hydride (53.0 mg, 2.21 mmol) and stirred for 4 h at room temperature. The resulting red solution was evaporated to dryness under reduced pressure and the residue was treated with toluene and filtered to remove the solids. The solution was again concentrated to ca. 0.5 mL, cooled to -40 °C and treated with hexane (3 mL) to give a red solid. The solid was separated by decantation, washed with cold hexane and dried in vacuo. Yield 105 mg (87 %). ^1H NMR (C_6D_6): $\delta = -10.21$ (tt, $^2J_{\text{H,P}} = 36.5$, $^2J_{\text{H,P}} = 14.0$, 1H, RuH), 0.27 (dd, $^3J_{\text{H,P}} = 12.9$, $^3J_{\text{H,H}} = 7.1$, 6H, PCHCH_3), 0.49 (dd, $^3J_{\text{H,P}} = 11.6$, $^3J_{\text{H,H}} = 7.2$, 6H, PCHCH_3), 0.80 (s, 6H, SiCH_3), 1.01 (dd, $^3J_{\text{H,P}} = 16.3$, $^3J_{\text{H,H}} = 7.4$, 6H, PCHCH_3), 1.07 (dd, $^3J_{\text{H,P}} = 9.6$, $^3J_{\text{H,H}} = 7.7$, 6H, PCHCH_3), 1.15 (m, 6H, PCHCH_3), 1.52 (m, 6H, PCHCH_3), 1.67 (dd, $^3J_{\text{H,P}} = 14.0$, $^3J_{\text{H,H}} = 7.0$, 6H, PCHCH_3), 1.71 (dd, $^3J_{\text{H,P}} = 16.8$, $^3J_{\text{H,H}} = 7.5$, 6H, PCHCH_3), 2.04, 2.51, 2.66, 2.72 (all m, 2H each, PCHCH_3), 6.99 (m, 4H, CH), 7.08, 7.23 (both m, 2H each, CH), 7.59 (br, 6H, CH), 7.92, 7.95 (both d, $^3J_{\text{H,H}} \approx 7.5$, 1H each, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 80.76$ (dd, $^2J_{\text{P,P}} = 13.9$, $^4J_{\text{P,P}} = 8.6$, 2P), 81.56 (dd, $^2J_{\text{P,P}} = 13.9$, $^4J_{\text{P,P}} = 8.6$, 2P). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 3.36$ (s, SiCH_3), 19.35, 19.77 (both brs, PCHCH_3), 19.96 (d, $^2J_{\text{C,P}} = 6.9$, PCHCH_3), 20.07 (d, $^2J_{\text{C,P}} = 10.2$, PCHCH_3), 20.71 (d, $^2J_{\text{C,P}} = 5.7$, PCHCH_3), 20.80 (d, $^2J_{\text{C,P}} = 1.8$, PCHCH_3), 23.27 (d, $^2J_{\text{C,P}} = 6.1$, PCHCH_3), 25.29 (br, PCHCH_3), 29.80 (br, PCHCH_3), 30.54 (d, $^1J_{\text{C,P}} = 16.8$, PCHCH_3), 31.82 (br, PCHCH_3), 37.60 (d, $^1J_{\text{C,P}} = 19.6$, PCHCH_3), 125.87 (br, CH), 126.32 (d, $J_{\text{C,P}} = 5.1$, CH), 126.75 (d, $^3J_{\text{C,P}} = 16.3$, CH), 128.66 (vbr, CH), 129.06 (br, CH), 131.24 (d, $^3J_{\text{C,P}} = 19.0$, CH), 131.54 (br, CH), 148.65 (d, $^1J_{\text{C,P}} = 41.6$, C), 160.20 (d, $^2J_{\text{C,P}} = 45.5$, C). The crystals used in the X-ray diffraction experiment were obtained from a benzene solution at room temperature.

$[\text{Ru}(\mu\text{-H})\{\kappa\text{P},\text{P},\text{Si-Si}(\text{Me})(\text{C}_6\text{H}_4\text{-2-PiPr}_2)_2\}_2]$ (7). The same procedure detailed for **6** but stirring for 18 h gave a red solid. Yield 70 mg (60 %). ^1H NMR ($[\text{D}_8]\text{toluene}$, 343 K): $\delta = -10.23$ (brt, $^1J_{\text{H,P}} \approx 31.4$, 2H, RuH), 0.23 (s, 6H, SiCH_3), 0.62, 0.83 (both br, 12H each, PCHCH_3), 1.16 (br, 24H, PCHCH_3), 2.06, 2.32 (both br, 4H each, PCHCH_3), 6.97 (m, 8H, CH), 7.33 (d, $^2J_{\text{H,H}} \approx 6.8$, 4H, CH), 7.84 (d, $^2J_{\text{H,H}} \approx 6.8$, 4H, CH). $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{toluene}$, 343 K): $\delta = 83.16$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{toluene}$, 343 K): $\delta = 1.37$ (s, SiCH_3), 19.90, 19.84, 20.72, 22.12 (all s, PCHCH_3), 29.28, 29.78 (both br, PCHCH_3), 125.84, 128.25, 131.58 (all s, CH), 148.31 (br, C), 159.77 (brd, $^2J_{\text{C,P}} = 42.7$, C). The crystals used in the X-ray diffraction experiment were obtained from a concentrated toluene solution stored at -20 °C.

Crystallography: X-ray data were collected at 100.0(2) K on a Bruker APEX DUO area detector diffractometer equipped with a normal focus, 2.4 kW, sealed tube source (molybdenum radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA. In all 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 30 (3, 5), or 40 (6) s, covering 0.3° in ω . Data were corrected for absorption by using a multi-scan method applied with the SADABS program.^[11] The structures were solved by the Patterson method and refined by full-matrix least squares on F^2 using the Bruker SHELXTL program package,^[12] including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen non-disordered atoms. Weighted R factors (R_w) and goodness of fit (S) are based on F^2 , and conventional R factors are based on F .

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1408088 (5), 1408089 (6) and 1408090 (7). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>)

Crystal data for 5. $\text{C}_{32}\text{H}_{45}\text{F}_3\text{O}_3\text{P}_2\text{SSiRu}$, $M = 757.84$; pale yellow irregular block, $0.14 \times 0.08 \times 0.04 \text{ mm}^3$; triclinic, $P-1$; $a = 9.7198(12) \text{ \AA}$, $b = 18.288(2) \text{ \AA}$, $c = 19.128(2) \text{ \AA}$; $\alpha = 98.006(2)$, $\beta = 95.413(2)$, $\gamma = 97.823(2)$; $Z = 4$; $V = 3313.3(7) \text{ \AA}^3$; $D_c = 1.519 \text{ g/cm}^3$; $\mu = 0.718 \text{ mm}^{-1}$, minimum and maximum transmission factors 0.888 and 1.000; $2\theta_{\text{max}} = 52.00$; 30903 reflections collected, 12998 unique [$R(\text{int}) = 0.1501$]; number of data/restraints/parameters 12998/286/861; final GoF 0.816, $R1 = 0.0603$ [12998 reflections $I > 2\sigma(I)$], $wR2 = 0.1999$ for all data; largest peak and hole 0.906 and $-1.153 \text{ e \AA}^{-3}$. Hydrogen atoms were calculated using a restricted riding model on their respective carbon atoms with the thermal parameter related to the bonded atom. The highest electronic residuals were observed in close proximity of a disordered triflate anion and make no chemical sense.

Crystal data for 6. $\text{C}_{50}\text{H}_{79}\text{ClP}_4\text{Si}_2\text{Ru}_2 \cdot 2(\text{C}_6\text{H}_6)$, $M = 1254.00$; red irregular block, $0.14 \times 0.08 \times 0.04 \text{ mm}^3$; triclinic, $P-1$; $a = 10.2846(6) \text{ \AA}$, $b = 14.0180(8) \text{ \AA}$, $c = 21.7503(13) \text{ \AA}$; $\alpha = 102.9700(10)$, $\beta = 95.3170(10)$, $\gamma = 93.4190(10)$; $Z = 2$; $V = 3032.1(3) \text{ \AA}^3$; $D_c = 1.374 \text{ g/cm}^3$; $\mu = 0.725 \text{ mm}^{-1}$, minimum and maximum transmission factors 0.854 and 0.912; $2\theta_{\text{max}} = 59.18$; 32077 reflections collected, 15394 unique [$R(\text{int}) = 0.0243$]; number of data/restraints/parameters 15394/180/693; final GoF 0.999, $R1 = 0.0267$ [13222 reflections $I > 2\sigma(I)$], $wR2 = 0.0676$ for all data; largest peak and hole 1.296 and $-0.444 \text{ e \AA}^{-3}$. Hydrogen atoms (except the hydride) were calculated using a restricted riding model on their respective carbon atoms with the thermal parameter related to the bonded atom. The hydride was refined freely. The highest electronic residuals were observed in close proximity of the Ru center and make no chemical sense.

Crystal data for 7. $\text{C}_{50}\text{H}_{80}\text{P}_4\text{Si}_2\text{Ru}_2 \cdot \text{C}_7\text{H}_8$, $M = 1155.48$; red irregular block, $0.14 \times 0.06 \times 0.04 \text{ mm}^3$; monoclinic, $P2_1/n$; $a = 18.2361(14) \text{ \AA}$, $b = 13.6890(10) \text{ \AA}$, $c = 23.6799(18) \text{ \AA}$; $\beta = 109.3380(10)$; $Z = 4$; $V = 5577.8(7) \text{ \AA}^3$; $D_c = 1.376 \text{ g/cm}^3$; $\mu = 0.735 \text{ mm}^{-1}$, minimum and maximum transmission factors 0.447 and 0.957; $2\theta_{\text{max}} = 52.00$; 50696 reflections collected, 10953 unique [$R(\text{int}) = 0.1213$]; number of data/restraints/parameters 10953/4/612; final GoF 0.741, $R1 = 0.0356$ [6078 reflections $I > 2\sigma(I)$], $wR2 = 0.0645$ for all data; largest peak and hole 0.742 and $-0.619 \text{ e \AA}^{-3}$. Hydride ligands were observed in the difference

Fourier maps but not refined properly, restrained geometries (the four Ru–H bond lengths were refined simultaneously) and thermal parameters were used for the last cycles of refinement. The rest of the hydrogen atoms were calculated and refined using a restricted riding model on their respective carbon atoms.

Supporting Information (see footnote on the first page of this article): NMR spectra for 2-7.

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Arene and Hydride Complexes of Ruthenium with *fac* PSiP Pincer

Ligands