Electronic Supplementary Information

Agostic Si-H Bond Coordination Assists C-H Bond Activation at Ruthenium in Bis(phosphinobenzylsilane) Complexes†

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Experimental Section

All manipulations were carried out under argon using standard Schlenk and glove box techniques. Solvents were dried with appropriate reagents and distilled prior to use. $RuH_2(\eta^2-H_2)_2(PCy_3)_2$ (**1**), Ru(COD)(COT) (**4**) and $Ph_2P(o-C_6H_4CH_2)SiMe_2H$ (**2**),were prepared according to reported procedures. Deuterated benzene, toluene and THF were dried over molecular sieves and degassed prior to use. NMR samples were all prepared under argon atmosphere using NMR tubes fitted with Teflon septa or Young's taps. NMR spectra were obtained on a Bruker DPX 300 (with ^1H at 300.13 MHz, ^{31}P at 121.49 MHz and ^{13}C at 75.46 MHz) and Bruker AMX 400 (with ^1H at 400.13 MHz, ^{31}P at 161.98 MHz, ^{13}C at 100.71 MHz and ^{29}Si at 79.50 MHz) spectrometers. Crystal data were collected at low temperature on a Xcalibur Oxford Diffraction diffractometer equipped with and Oxford Cryosystems cryostream cooler device and using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Microanalyses were obtained on an Elementar Vario EL III instrument in the CHNS operation mode.

Synthesis of $RuH_2\{\eta^2-(H-SiMe_2)-o-CH_2(C_6H_4)PPh_2\}_2$ (3). In situ addition of $Ph_2P(o-C_6H_4CH_2)SiMe_2H$ (**2**, 21 mg,0.062 mmol)to $RuH_2(\eta^2-H_2)_2(PCy_3)_2$ (**1**, 20 mg, 0.03 mmol) in toluene-d_8 in an NMR tube resulted in immediate gas evolution, total dissolution of the solid and a change of colour from light pink to orange. The NMR spectra recorded a few minutes after showed total conversion to **3**. ^1H NMR (300 MHz, toluene-d_8, 193 K): δ -10.45 (AA'XX' multiplet $\omega_{1/2}$ = 94 Hz with the two main lines separated by Δ = 30Hz, 2H, J_{SiH} 15 Hz, Ru*H*), -5.16 (br s, $\omega_{1/2}$ = 40 Hz, 2H, J_{SiH} 27.8 Hz, η^2-SiH), 0.74 (m, 6H, $Si(CH_3)_2$), 2.13 (s, 2H, Ru-C*H*), 6.89-6.92 (m, 6H, arom), 7.10 (m, 8H, arom), 7.18 (m, 2H, arom),7.41 (m, 4H, arom), 7.46 (m, 2H, arom), 7.55 (m, 4H, arom), 7.68 (m, 2H, arom). $^{31}P\{^1H\}$ NMR (121.49 MHz, toluene-d_8, 193 K): δ 39.2(s). $^{29}Si\{^1H, ^{31}P\}$ NMR (79.46 MHz, toluene-d_8, 193 K): δ + 8.30(s). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6, 298 K): δ -3.67 (s, $Si(CH_3)_2$), -2.51 (s, $Si(CH_3)_2$), 24.76 (m, J_{CH} 140.9 Hz, CH), 121.28 (m, arom), 127.24 (m, arom), 127.69 (m, arom), 128.12 (s, arom), 128.16 (m, arom), 129.03 (s, arom), 129.07 (s, arom), 131.95 (m, arom), 133.23 (s, arom), 134.44 (m, arom), 137.10 (m, C_{ipso}), 138.20 (m, C_{ipso}), 163.69 (m, C_{ipso}). Leaving the mixture to stand for hours showed also resonances due to **6** and eventually after days, **5** was also observed.

Synthesis of Ru[η^2-H-SiMe$_2$(CH(C$_6$H$_4$)PPh$_2$]$_2$ (5). Ru(COD)(COT)(160 mg, 0.51 mmol) and $Ph_2P(o-C_6H_4CH_2)SiMe_2H$ (341 mg, 1.02 mmol) in ca. 8 ml pentane were stirred at room temperature for 3 h. The initially yellow solution evolved to a white-yellowish precipitate which was subsequently filtered, washed three times with 1 ml of cold pentane and dried under vacuum. The NMR spectra of the light yellow solid showed only resonances due to **5**. Yield 92%. Elemental analysis calcted. for $RuC_{42}H_{44}P_2Si_2$: C, 65.71, H, 5.74. Found: C, 65.66, H, 5.66. Crystals of **5** can be grown from concentrated hexane or pentane solutions at -30 °C. Alternatively, slow diffusion of hexane into toluene solutions of compound **2** also rendered crystals of **5**.

^{1}H NMR (400 MHz, benzene-d$_6$, 293 K): δ -9.77 (t, J_{PH} 38 Hz, J_{SiH} 67Hz, 2H, η^2-SiH), -0.33 (s, 6H, Si(CH_3)$_2$), 0.77 (s, 6H, Si(CH_3)$_2$), 2.15 (s, 2H, Ru-CH), 6.89-6.92 (m, 6H, arom), 7.10 (m, 8H, arom), 7.18 (m, 2H, arom),7.41 (m, 4H, arom), 7.46 (m, 2H, arom), 7.55 (m, 4H, arom), 7.68 (m, 2H, arom). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d$_6$, 298 K): δ 56.92 (s). ^{29}Si{^{1}H,^{31}P} NMR (79.46 MHz, toluene-d$_8$, 193 K): δ -4.37(s). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d$_6$, 298 K): δ -3.67 (s, Si(CH_3)$_2$), -2.51 (s, Si(CH_3)$_2$), 24.76 (m, J_{CH} 140.9 Hz, CH), 121.28 (m, arom), 127.24 (m, arom), 127.69 (m, arom), 128.12 (s, arom), 128.16 (m, arom), 129.03 (s, arom), 129.07 (s, arom), 131.95 (m, arom), 133.23 (s, arom), 134.44 (m, arom), 137.10 (m, C_{ipso}), 138.20 (m, C_{ipso}), 163.69 (m, C_{ipso}).

Reaction of Ru(COD)(COT) with 2 eq Ph$_2$P(*o*-C$_6$H$_4$CH$_2$)SiMe$_2$H under H2: Formation of RuH{η^2-(H$\tilde{}$SiMe$_2$)-*o*-CH$_2$(C$_6$H$_4$)PPh$_2$}{η^2-(H$\tilde{}$SiMe$_2$)-*o*-CH(C$_6$H$_4$)PPh$_2$} (6). $Ph_2P(o-C_6H_4CH_2)SiMe_2H$ (341 mg, 1.02 mmol) in ca. 8 ml pentane were added under dihydrogen to a Fischer-Porter bottle containing Ru(COD)(COT)(160 mg, 0.51 mmol) and the mixture was pressurized to 3 bar with H_2. A precipitate was formed and the reaction left to stir for a total of 2 h. The solid was then washed three times with cold pentane and dried under a slight vacuum. The NMR spectra of the yellow solid was indicative of a mixture of **3**, **6** and **5** in approximate ratio 1:13:5 as determined by the integrations in the ^{1}H NMR spectrum. As expected, leaving the mixture to stand for longer times caused variations in the ratio of the products. Complex **6**, selected ^{1}H NMR data (400 MHz, toluene-d$_8$, 298 K) δ -6.04 (br s, J_{HSi} = 76Hz, 1H), -8.00 (pt, $^2J_{H-P}$ = 21 and 27 Hz, J_{HSi} = 27 Hz, 1H), -9.36 (dd, $^2J_{H-P}$ = 24 and 54 Hz, J_{HSi} = 40 Hz, 1H). ^{31}P{^{1}H} NMR

(161.92 MHz, toluene-d_6, 298 K): δ 56.51 (d, $^2J_{P-P}$ 21 Hz), 42.70 (d, $^2J_{P-P}$ = 21 Hz). ^{29}Si{^{1}H,^{31}P} NMR (79.46 MHz, toluene-d_8, 193 K): δ -13.00 (s), +11.00 (s).

Computational details

DFT calculations were performed with the GAUSSIAN 03 series of programs[1] using the non-local hybrid functional denoted as B3PW91.[2] For ruthenium, the core electrons were represented by a relativistic small core pseudopotential using the Durand-Barthelat method[3] . The 16 electrons corresponding to the 4s, 4p, 4d and 5s atomic orbitals were described by a (7s, 6p, 6d) primitive set of Gaussian functions contracted to (5s, 5p, 3d). Standard pseudopotentials developed in Toulouse were used to describe the atomic cores of all other non-hydrogen atoms (C, Si and P).[4] A double plus polarization valence basis set was employed for C, Si and P (d-type function exponents were 0.80, 0.45 and 0.45, respectively). For hydrogen, a standard primitive (4s) basis contracted to (2s) was used. A p type polarization function (exponent 0.9) was added for the hydrogen atoms directly bound to ruthenium and silicon. The geometry of the various critical points on the potential energy surface was fully optimized with the gradient method available in GAUSSIAN 03. Calculations of harmonic vibrational frequencies were performed to determine the nature of each critical point.

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Table S1: Cartesian Coordinates (Å) of the *trans* $RuH_2\{\eta^2\text{-}(H{-}SiMe_2)\text{-}o\text{-}CH_2(C_6H_4)PH_2\}_2$ **(3a)** calculated at DFT/B3PW91 (relative energy E= -236.794841 a. u. and relative free energy G= -236.411608 a. u).

Ru	0.000000	0.000000	0.098308
H	-1.160438	-0.024100	1.285463
H	1.160438	0.024100	1.285463
Si	-0.982270	-1.819832	1.525204
Si	0.982270	1.819832	1.525204
H	-1.051451	-0.717916	-0.923190
H	1.051451	0.717916	-0.923190
C	-0.085053	3.421957	1.281247
C	0.085053	-3.421957	1.281247
C	-0.067277	4.006810	-0.103851
C	0.067277	-4.006810	-0.103851
C	-0.627876	3.297257	-1.201541
C	0.627876	-3.297257	-1.201541
P	-1.281105	1.610369	-0.929861
P	1.281105	-1.610369	-0.929861
C	0.530976	5.261312	-0.359438
C	-0.530976	-5.261312	-0.359438
C	-0.567119	-5.804666	-1.651579
C	0.567119	5.804666	-1.651579
C	0.000000	5.102336	-2.728666
C	0.000000	-5.102336	-2.728666
C	-0.590582	3.851326	-2.499785
C	0.590582	-3.851326	-2.499785
H	-2.574634	1.878674	-0.366245
H	2.574634	-1.878674	-0.366245
H	-1.722615	1.341253	-2.262226
H	1.722615	-1.341253	-2.262226
H	-0.304500	-4.164625	2.006649
H	0.304500	4.164625	2.006649
H	-1.117858	3.175297	1.606538
H	1.117858	-3.175297	1.606538
C	2.745914	2.317071	1.055460
C	-2.745914	-2.317071	1.055460
C	0.933729	1.616542	3.410062
C	-0.933729	-1.616542	3.410062
H	3.455151	1.488718	1.255069
H	-3.455151	-1.488718	1.255069
H	2.816714	2.569508	-0.020391
H	-2.816714	-2.569508	-0.020391
H	-3.078203	-3.200769	1.638046
H	3.078203	3.200769	1.638046
H	1.597198	0.796343	3.748700
H	-1.597198	-0.796343	3.748700
H	1.270160	2.551614	3.903572

H	-1.270160	-2.551614	3.903572
H	-0.089147	1.390416	3.769665
H	0.089147	-1.390416	3.769665
H	1.022661	-3.296909	-3.340687
H	-1.022661	3.296909	-3.340687
H	-0.019559	-5.523481	-3.739083
H	0.019559	5.523481	-3.739083
H	-1.036051	-6.780454	-1.818297
H	1.036051	6.780454	-1.818297
H	0.968955	5.817460	0.477244
H	-0.968955	-5.817460	0.477244

Table S2: Cartesian Coordinates (Å) of the *cis* $RuH_2\{\eta^2\text{-}(H\text{–}SiMe_2)\text{-}o\text{-}CH_2(C_6H_4)PH_2\}_2$ **(3b)** calculated at DFT/B3PW91 (relative energy E= -236.807645 a. u. and relative free energy G= -236.425606 a. u).

Ru	0.000000	0.000000	0.469922
H	-1.161857	-1.133437	0.200862
H	1.161857	1.133437	0.200862
Si	-0.407648	-2.045076	1.747882
Si	0.407648	2.045076	1.747882
H	-1.062613	0.470120	1.602691
H	1.062613	-0.470120	1.602691
C	-0.709475	3.428542	0.995913
C	0.709475	-3.428542	0.995913
C	-0.466740	3.784930	-0.449857
C	0.466740	-3.784930	-0.449857
C	-0.762109	2.871968	-1.503874
C	0.762109	-2.871968	-1.503874
P	-1.312210	1.173422	-1.085552
P	1.312210	-1.173422	-1.085552
C	0.072154	5.044024	-0.798063
C	-0.072154	-5.044024	-0.798063
C	-0.308033	-5.399587	-2.134313
C	0.308033	5.399587	-2.134313
C	0.000000	4.499579	-3.167289
C	0.000000	-4.499579	-3.167289
C	-0.531960	3.241777	-2.847019
C	0.531960	-3.241777	-2.847019

H	-2.698385	1.373679	-0.767625
H	2.698385	-1.373679	-0.767625
H	-1.520892	0.670325	-2.413715
H	1.520892	-0.670325	-2.413715
H	0.566456	-4.328276	1.627864
H	-0.566456	4.328276	1.627864
H	-1.760153	3.101299	1.150867
H	1.760153	-3.101299	1.150867
C	2.168534	2.757619	1.814915
C	-2.168534	-2.757619	1.814915
C	-0.090941	1.953751	3.576261
C	0.090941	-1.953751	3.576261
H	2.878868	1.996442	2.197168
H	-2.878868	-1.996442	2.197168
H	2.523230	3.075304	0.814262
H	-2.523230	-3.075304	0.814262
H	-2.213341	-3.634152	2.493901
H	2.213341	3.634152	2.493901
H	0.498413	1.176359	4.101026
H	-0.498413	-1.176359	4.101026
H	0.112911	2.924991	4.073084
H	-0.112911	-2.924991	4.073084
H	-1.163093	1.709403	3.707394
H	1.163093	-1.709403	3.707394
H	0.767771	-2.536668	-3.652057
H	-0.767771	2.536668	-3.652057
H	-0.171922	-4.772529	-4.213529
H	0.171922	4.772529	-4.213529
H	-0.727028	-6.383996	-2.369124
H	0.727028	6.383996	-2.369124
H	0.303114	5.756936	0.001528

Table S3: Cartesian Coordinates (Å) of the *cis* $RuH_2\{\eta^2\text{-}(H\text{–}SiMe_2)\text{-}o\text{-}CH(C_6H_4)PH_2\}_2$ (**5a**) calculated at DFT/B3PW91 (relative energy E=-234.451508 a. u. and relative free energy G= -234.106909 a. u).

C	-2.626948	-1.466648	-2.397795
C	-1.822509	-1.374618	-1.234342
C	-1.146123	-2.549503	-0.821402
C	-1.310760	-3.773130	-1.496764
C	-2.124986	-3.843889	-2.635704
C	-2.771035	-2.676474	-3.088771
C	-1.716539	-0.122995	-0.441620
Si	-2.457361	-0.076907	1.250898
C	-3.364817	-1.608897	1.856776
P	0.000000	-2.271796	0.575357
Ru	0.000000	0.000000	0.977757
Si	2.457361	0.076906	1.250898
C	3.364817	1.608896	1.856777
P	0.000000	2.271796	0.575357
C	1.146123	2.549503	-0.821402
C	1.822509	1.374618	-1.234342
C	2.626948	1.466648	-2.397795
C	2.771036	2.676474	-3.088770
C	2.124987	3.843889	-2.635703
C	1.310760	3.773130	-1.496763
C	1.716539	0.122995	-0.441620
C	3.468019	-1.428465	1.758272
C	-3.468019	1.428464	1.758272
H	-1.131435	-0.000934	2.296342
H	1.131435	0.000933	2.296342
H	0.339722	3.305142	1.514396
H	-0.339722	-3.305142	1.514396
H	-1.207928	2.882340	0.105931
H	1.207928	-2.882340	0.105931
H	1.896889	-0.770782	-1.061306
H	-1.896889	0.770782	-1.061306
H	0.779598	4.667828	-1.149050
H	-0.779597	-4.667828	-1.149051
H	2.242232	4.789323	-3.175058
H	-2.242231	-4.789323	-3.175059
H	3.395834	2.714607	-3.988237
H	-3.395833	-2.714607	-3.988238
H	3.148533	0.570470	-2.754357
H	-3.148533	-0.570470	-2.754357
H	3.629519	-1.428836	2.855221
H	-3.629519	1.428835	2.855221

H	2.991034	-2.386827	1.484962
H	-2.991034	2.386826	1.484962
H	4.462629	-1.392855	1.269466
H	-4.462629	1.392854	1.269466
H	4.408267	1.595198	1.482075
H	-4.408267	-1.595199	1.482074
H	2.901828	2.550858	1.509616
H	-2.901828	-2.550859	1.509615
H	3.399420	1.629033	2.964538
H	-3.399420	-1.629034	2.964537

Table S4: Cartesian Coordinates (Å) of the *trans* $RuH_2\{\eta^2\text{-}(H\text{–}SiMe_2)\text{-}o\text{-}CH(C_6H_4)PH_2\}_2$ (**5b**) calculated at DFT/B3PW91 (relative energy E=-234.457744 a. u and relative free energy G= -234.114128 a. u).

C	3.007783	-0.107137	0.578840
C	3.285884	-0.222157	-0.808421
C	4.586556	-0.487071	-1.276624
C	5.639414	-0.684006	-0.372087
C	5.375868	-0.609772	1.009561
C	4.086318	-0.321272	1.474015
P	1.797913	-0.083465	-1.871717
H	1.957497	-1.178548	-2.781665
C	1.649309	0.250262	1.069138
Si	0.944713	1.915846	0.780434
C	-0.002312	2.742745	2.176277
Ru	0.000057	-0.000197	-0.427423
Si	-0.944974	-1.915777	0.780955
C	-2.022564	-3.197903	-0.074779
P	-1.797766	0.082567	-1.871792
C	-3.285704	0.222018	-0.808542
C	-3.007629	0.107523	0.578772
C	-4.086123	0.322287	1.473849
C	-5.375607	0.610874	1.009267
C	-5.639135	0.684572	-0.372413
C	-4.586317	0.487018	-1.276861
C	-1.649236	-0.249963	1.069226
H	-1.957180	1.177237	-2.782265
C	2.022086	3.197985	-0.075562
C	0.001632	-2.742651	2.177082
H	2.157451	0.937969	-2.816844
H	-2.157476	-0.939267	-2.816420
H	-1.404916	-4.007105	-0.513625
H	-2.713551	-3.656546	0.660936

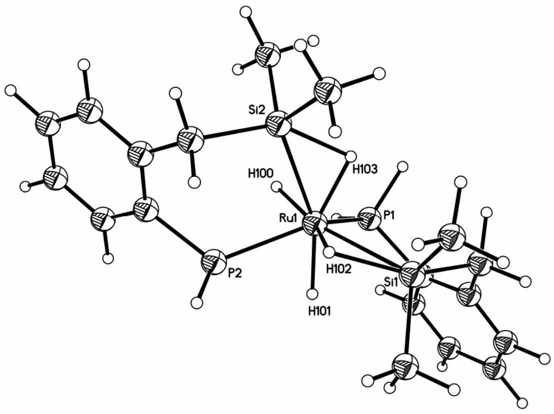
H	-0.688881	-3.373199	2.772505
H	0.804666	-3.395614	1.781408
H	-2.639488	-2.759214	-0.880812
H	0.467744	-2.006340	2.855843
H	6.647977	-0.906622	-0.735216
H	0.226772	-1.693707	-0.442843
H	6.186011	-0.774952	1.728835
H	4.773238	-0.565349	-2.354816
H	3.900378	-0.250440	2.552466
H	1.447846	-0.148911	2.075194
H	-3.900201	0.251886	2.552331
H	-1.447782	0.149408	2.075205
H	-6.185715	0.776546	1.728468
H	-4.772976	0.564877	-2.355087
H	-6.647647	0.907257	-0.735640
H	-0.226620	1.693264	-0.443725
H	-0.464746	2.006326	2.857439
H	2.638363	2.759410	-0.882151
H	0.687086	3.376891	2.769156
H	-0.808255	3.392100	1.780598
H	2.713673	3.656216	0.659845
H	1.404347	4.007483	-0.513743

Table S5: Cartesian Coordinates (Å) of RuH{η^2-(H−SiMe$_2$)-o-CH$_2$(C$_6$H$_4$)PPh$_2$}{η^2-(H−SiMe$_2$)-o-CH(C$_6$H$_4$)PPh$_2$} (**6**) calculated at DFT/B3PW91 (relative energy E=-235.680896 a. u. and relative free energy G= -235.319663 a. u).

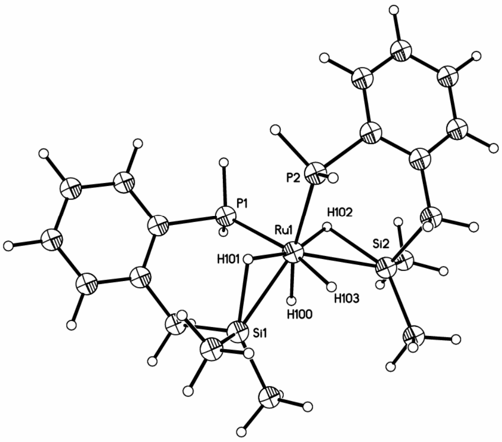
C	-2.735644	0.716066	0.708611
C	-2.435583	1.795710	-0.162136
C	-3.172204	2.995170	-0.127959
C	-4.203819	3.165487	0.805380
C	-4.492594	2.119351	1.703485
C	-3.776119	0.917435	1.650851
P	-0.986704	1.495583	-1.239974
Ru	-0.079814	-0.540307	-0.521027
Si	-2.234770	-1.694990	-0.824990
C	-2.314404	-3.540827	-0.489645
C	-2.013024	-0.580742	0.620640
P	1.905057	-0.509675	-1.708358
C	3.314675	0.321542	-0.866016
C	3.994550	1.383905	-1.492702
C	4.982331	2.112288	-0.811430

C	5.290892	1.772889	0.514547
C	4.622709	0.708062	1.138707
C	3.630183	-0.040277	0.472216
C	2.937143	-1.178981	1.170522
Si	1.062250	-0.969026	1.574523
C	0.923948	0.352437	2.936335
C	0.601438	-2.576437	2.489099
C	-3.519089	-1.210468	-2.113257
H	2.494070	-1.759147	-2.096562
H	-0.238237	2.710190	-1.137704
H	2.013295	0.118920	-2.990709
H	-1.490848	1.736552	-2.562622
H	-3.353709	-1.752634	-3.064091
H	-4.532105	-1.466833	-1.747552
H	-3.349175	-3.847806	-0.243845
H	-1.991616	-4.118783	-1.376764
H	-3.511174	-0.127041	-2.330316
H	-1.658379	-3.818941	0.353986
H	5.502433	2.935400	-1.312286
H	-0.830464	-1.490847	-1.780346
H	6.055688	2.332820	1.063545
H	3.747690	1.652055	-2.526841
H	4.878639	0.441186	2.171039
H	3.452107	-1.391690	2.125331
H	-4.023254	0.106478	2.346296
H	-1.996066	-1.109269	1.586578
H	-5.286770	2.243835	2.448197
H	-2.921216	3.810953	-0.816924
H	-4.765788	4.104102	0.845107
H	0.365440	-2.011316	0.014730
H	0.834741	-3.478510	1.891932
H	1.405238	1.303937	2.639863
H	1.156156	-2.642781	3.446347
H	-0.477342	-2.609395	2.734409
H	1.397763	0.003755	3.875481
H	-0.137887	0.574617	3.156017
H	3.019080	-2.104422	0.566859
H	0.581161	0.540080	0.494106

`Optimized geometries by DFT (B3PW91) of isomers 3a and 3b.`

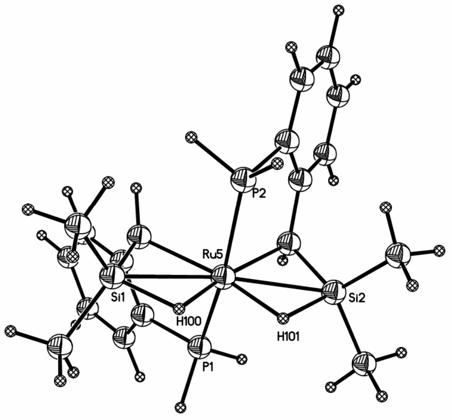


Isomer 3a

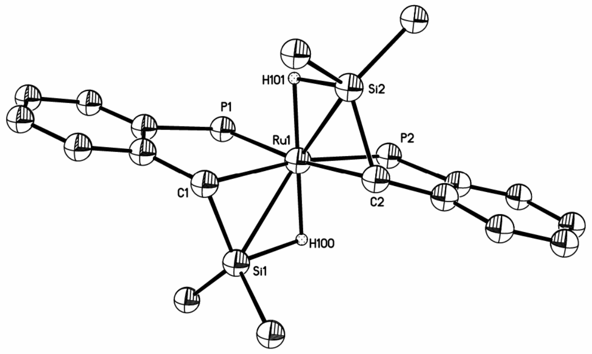


Isomer 3b

Optimized geometries by DFT (B3PW91) of isomers 5a and 5b



Isomer 5a



Isomer 5b (non relevant H atoms omitted for clarity)

Optimized geometry by DFT (B3PW91) of 6 (non relevant H atoms omitted for clarity)