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σ-Silane Ruthenium Complexes: The Crucial Role of Secondary Interactions

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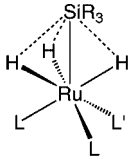
On pages 2118–2120 of the original article,[1] the references in Tables 1 and 2 are incorrect as a result of an inadvertent error during the revision of the article, and in Figure 6 on page 2121 of the same article,[1] the ligand L′ was omitted; the correct version of Tables 1 and 2 and Figure 6 are given.



L, L' = phosphane, CO, σ-H_2
R = alkyl, aryl, alkoxy, amino or halogen

Figure 6. Schematic representation of a series of complexes of general formula $RuH_3(SiR_3)L_2L'$.

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Table 1. Selected NMR and IR data[a] for various silane and silyl ruthenium complexes.

	Formula	$\delta = {}^{1}H$ [ppm]	J_{SiH} [Hz]	$\delta = {}^{29}Si$ [ppm]	$\nu_{Ru-H-Si}$ [cm^{-1}]	ν_{Ru-H} [cm^{-1}]	Ref.
2	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(C_6H_4)](PCy_3)_2$	–7.74 (t) –12.03 (m)	65	4.8	1778	1969 1985	[18,19]
3a	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(CH_2)_2](PCy_3)_2$	–8.21 (t) –12.65 (m)	70	12.2	1773	1981 2012	[18]
3b	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(CH_2)_2](PCy_3)(PPh_3)$	–7.68 (t) –11.10 (dd) –11.47 (dd)	64	14.7	1768	 1989 2008	[18]
3c	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(CH_2)_2](PPh_3)_2$	–7.60 (t) –10.92 (m)	64	16.4	1797	1961 1978	[18]
4	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(CH_2)_3](PCy_3)_2$	–8.49 (t) –12.17 (m)	75	–11.1	1803	1961 1994	[18]
5	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(OSiMe_2O)](PCy_3)_2$	–9.14 (t) 11.20 (m)	82	4.9	1798	1955 2045	[18]
6	$RuH_2[(\eta^2\text{-}HSiMe_2)_2NH](PCy_3)_2$	–8.36 (br.) –8.62 (br.) –9.93 (br.) –10.76 (br.)	–	–	1712	 1972 2040	[20]
7	$RuH_2[(\eta^2\text{-}HSiMe_2)_2O](PCy_3)_2$	–8.1 (br.) –8.5 (br.) –9.4 (br.) –10.2 (br.)	22 (av.)[b]	–5.61	1699	 1969 2045	[18,19]
8a	$RuH_2[(\eta^2\text{-}HSiPh_2)_2O](PCy_3)_2$ (sym)	–7.67 (br.) –9.70 (t)	41 (av.)[b]	4.80	1670	1976 2019	[14,18]
8b	$RuH_2[(\eta^2\text{-}HSiPh_2)_2O](PCy_3)_2$ (non sym)	–7.08 (br.) –8.11 (br.) –8.99 (br. t) –9.81 (br. t)					
9a	$RuH_2[(\eta^2\text{-}HSiPh_2)\text{–}O\text{–}(SiHPh_2)](PPh_3)_3$	–8.97 (dt, 1 H) –9.40 (br. t, 2 H)	35 (av.)[b]	11.7 –21.4 (free)	–	–	[14]
9b	$RuH_2[(\eta^2\text{-}HSiPh_2)\text{–}O\text{–}(Si(OH)Ph_2)](PPh_3)_3$	–9.15 (m, 3 H)	–	–	–	–	[14]
10	$RuH_3(SiCl_2Me)(PPh_3)_3$	–9.76 (m)	39.7 (av.)[b]	36.4	–	1961.5	[21]
11	$RuH_3(SiPyr_3)(PPh_3)_3$	–9.80 (m)	47.4 (av.)[b]	8.6	–	1960 1969	[23]
12a	$RuH_3(SiMe_3)(PMe_3)_3$	–10.18 (br. m)	–	–10.8	–	1887 (av.)	[27]
12b	$RuH_3(SiEt_3)(PMe_3)_3$	–10.53 (br. m)	–	12.7	–	1897 (av.)	[27]
12c	$RuH_3(SiMe_2CH_2SiMe_3)(PMe_3)_3$	–10.15 (br. m)	25	–9.2 –0.9 (free)	–	1898 (av.)	[22]
13	$RuH_2(\eta^2\text{-}HSiPh_3)(\eta^2\text{-}H_2)(PCy_3)_2$	–8.3 (br. s)	18 (av.)[b]	5.7	–	–	[28]
14	$RuH_2(\eta^2\text{-}HSiMe_2Cl)(\eta^2\text{-}H_2)(PCy_3)_2$	–8.51 (br. s)	–	38	–	–	[29]
15	$RuH_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2$	–8.77 (br.) –9.46 (dt) –12.46 (dt)	105	–11.3	–	1945 2021	[32]
16	$RuCl(H)(\text{–}CH_2SiMe_2)(PMe_3)_3$ (*fac*)	–7.7 (dt)	75.0	–19.4	1615	–	[33]
	$RuCl(H)(\text{–}CH_2SiMe_2)(PMe_3)_3$ (*mer*)	–6.0 (dt)	77.5	–19.8	–	–	[33]
17	$RuH(\eta^2\text{-}HSiEt_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$	–9.54 (br. t) –12.63 (dd)	36.7 24.7	–	–	–	[38]
18	$RuH(\eta^2\text{-}HSiMe_2Et)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$	–9.45 (ps t) –12.46 (dd)	40.1 24.1	5.0	–	–	[37]
19	$RuH(\eta^2\text{-}HSiMe_2Cl)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$	–9.06 (ps t) –11.98 (dd)	37.3 24.1	46.2	–	–	[29]
20	$Cp^*RuCl(\eta^2\text{-}HSiClMe_2)(P\mathit{i}Pr_3)$	–9.65 (t)	33.5	–	1916	–	[35]
21	$[CpRuH(SiCl_3)(PMe_3)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$	–9.87 (t)	48	30.6	–	–	[39]
22	$Ru_2H_4(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}SiH_4)(PCy_3)_4$	–6.0 (br.) –8.6 (br.)	36 (av.)[b]	290.2	1667	1911	[40,41]
23	$Ru_2H_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si(OMe)_2]_3(PCy_3)_2$	–9.94 (br.)	22 (av.)[b]	85.7	1703	1899 2022	[41]
24	$[Cp^*RuH]_2(\eta^2\text{:}\eta^2\text{-}H_2Si\mathit{t}Bu_2)$	–6.15 (s) –16.63 (s)	75	75.5	1790	–	[42]
25a	$[Cp^*Ru(CO)]_2(\eta^2\text{:}\eta^2\text{-}H_2Si\mathit{t}Bu_2)$	–13.60 (s)	22.4	186.2	–	–	[42]
25b	$[Cp^*Ru(CO)]_2(\eta^2\text{:}\eta^2\text{-}HSi\mathit{t}Bu_2)H$	–11.79 (s) –14.40 (s)	31.6	168.2	–	–	[42]
26a	$[Cp^*Ru]_2(\mu\text{-}\eta^2\text{-}HSi\mathit{t}Bu_2)(\mu\text{-}\eta^2\text{-}HSiPhH)(\mu\text{-}H)H$	–11.64 (s) –12.84 (s) –14.00 (s) –16.46 (s)	26 49 	–	1813 1613 	2054 	[42]
26b	$[Cp^*Ru]_2(\mu\text{-}\eta^2\text{-}HSi\mathit{t}Bu_2)(\mu\text{-}\eta^2\text{-}HSiEtH)(\mu\text{-}H)H$	–12.32 (s) –13.26 (s) –14.29 (s) –16.67 (s)	–	–	1835 1659	2062 	[42]

[a] NMR/IR data were obtained under the following conditions: **2**–**5**,**12**,**17**,**23**, C_6D_6, room temp./Nujol mull; **6**,**8**,**9a**,**22**, C_7D_8, 193 K/Nujol mull; **7**, C_7D_8, 178 K/Nujol mull; **9b**,**11**,**13**–**15**,**18**–**19**, C_7D_8, room temp./Nujol mull; **10**, CD_2Cl_2, room temp./KBr; **16**, C_7D_8, 301 K/Fluorolube; **20**, C_7D_8, 233 K/Nujol mull; **21**, CD_2Cl_2, 298 K; **24**–**26**, C_7D_8, 298 K/KBr. [b] J_{SiH} values were determined at room temperature. Average values involving all the hydrides and dihydrogen ligand in the case of **13**.

Table 2. Selected interatomic distances [Å] for various silane and silyl ruthenium complexes.

	Formula	Ru–Si		Si–H		Si···H		Ref.
		X-Ray	DFT[a]	X-Ray	DFT[a]	X-Ray	DFT[a]	
2	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(C_6H_4)](PCy_3)_2$	2.425(1)	2.425	1.84(2)	1.848	2.22(2)	2.253	[18,19]
						2.18(2)	2.253	
		2.429(2)	2.425	1.84(2)	1.848	2.12(2)	2.253	
						2.21(2)	2.253	
3a	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(CH_2)_2](PCy_3)_2$	2.428(1)	2.441	1.73(3)	1.853	2.27(3)	2.22	[18]
						2.13(3)	2.329	
		2.411(1)	2.441	1.78(3)	1.853	2.12(3)	2.329	
						2.31(3)	2.22	
5	$RuH_2[(\eta^2\text{-}HSiMe_2)_2(OSiMe_2O)](PCy_3)_2$	2.484(1)	2.451	1.77(4)	1.826	2.25(3)	2.170	[18]
						2.43(3)	2.484	
		2.434(1)	2.447	1.81(3)	1.839	2.32(3)	2.426	
						2.04(3)	2.168	
6	$RuH_2[(\eta^2\text{-}HSiMe_2)_2NH](PCy_3)_2$	2.395(2)	2.416	1.93(5)	1.922	2.35(6)	2.510	[20]
						2.25(6)	2.191	
		2.434(2)	2.490	1.91(5)	1.775	2.39(5)	2.500	
						2.09(6)	2.367	
9b	$RuH_2[(\eta^2\text{-}HSiPh_2)\text{–}O\text{–}(Si(OH)Ph_2)](PPh_3)_3$	2.356(2)	–	1.97(5)	–	2.03(5)	–	[14]
						2.07(5)		
10	$RuH_3(SiCl_2Me)(PPh_3)_3$	2.2760(4)	–	–	–	1.86(2)	–	[21]
						1.94(2)		
						1.94(3)		
12a	$RuH_3(SiMe_3)(PMe_3)_3$	2.376(1)	–	–	–	2.13(5)	–	[27]
						2.18(5)		
						2.23(5)		
12c	$RuH_3(SiMe_2CH_2SiMe_3)(PMe_3)_3$	2.3774(8)	–	–	–	2.00(4)	–	[22]
						2.09(4)		
						2.05(5)		
12d	$RuH_2(SiMe_2CH_2CH_2SiMe_2)(PMe_3)_3$	2.4682(9)	–	1.81(4)	–	–	–	[22]
		2.4514(9)						
13	$RuH_2(\eta^2\text{-}HSiPh_3)(\eta^2\text{-}H_2)(PCy_3)_2$	2.385(2)	2.394	1.72(3)	1.946	1.83(3)	2.071	[25]
						2.40(4)	2.116	
15	$RuH_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2$	2.498(2)	2.499	1.59(8)	1.658	–	–	[32]
16	$RuCl(H)(\text{–}CH_2SiMe_2)(PMe_3)_3$ (*fac*)	2.526(2)	–	1.664	–	–	–	[27]
16	$RuCl(H)(\text{–}CH_2SiMe_2)(PMe_3)_3$ (*mer*)	2.468(2)	–	1.557	–	–	–	[27]
18	$RuH(\eta^2\text{-}HSiMe_2Et)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$	2.418 (1)	2.468	–	1.847	–	2.164	[37]
19[b]	$RuH(\eta^2\text{-}HSiMe_2Cl)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$	2.353 (2)	2.398	1.91 (2)	1.891	1.99(2)	2.076	[29]
20	$Cp^*RuCl(\eta^2\text{-}HSiClMe_2)(P\mathit{i}Pr_3)$	2.398(1)	2.427	2.05	2.072	–	–	[35]
21	$[CpRuH(SiCl_3)(PMe_3)_2]^+$	2.329(1)	–	1.77(5)	–	–	–	[39]
22	$Ru_2H_4(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}SiH_4)(P\mathit{i}Pr_3)_4$	2.1875(4)	2.229	1.69(3)	1.685	–	–	[41]
				1.73(3)	1.685			
23	$Ru_2H_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2Si(OMe)_2]_3(PCy_3)_2$	2.456(3)	2.486	–	in the range	–	–	[41]
		2.364(3)	2.398		1.654–1.760			
		2.408(3)	2.551					
		2.419(3)	2.551					
		2.355(3)	2.400					
		2.408(3)	2.487					

[a] All the calculations were carried out at the B3LYP level of theory, except for compounds **2**, **6** (B3PW91) and **20** (BP86), by using the following model compounds: **2** $RuH_2[(\eta^2\text{-}HSiH_2)_2(C_6H_4)](PH_3)_2$, **3a** $RuH_2[(\eta^2\text{-}HSiH_2)_2(CH_2)_2](PH_3)_2$, **5** $RuH_2[(\eta^2\text{-}HSiH_2)_2(OSiH_2O)](PH_3)_2$, **6** $RuH_2[(\eta^2\text{-}HSiMe_2)_2NH](PCy_3)_2$, **13** $RuH_2(\eta^2\text{-}HSiH_3)(\eta^2\text{-}H_2)(PH_3)_2$, **15** $RuH_2\{\eta^4\text{-}HSiH_2(CH{=}CHMe)\}(PH_3)_2$, **18** $RuH(\eta^2\text{-}HSiMe_3)\{(\eta^3\text{-}C_6H_8)PH_2\}(PH_3)$, **19** $RuH(\eta^2\text{-}HSiMe_2Cl)\{(\eta^3\text{-}C_6H_8)PH_2\}(PH_3)$, **20** $Cp^*RuCl(\eta^2\text{-}HSiClMe_2)(P\mathit{i}Pr_3)$, **22** $Ru_2H_4(\mu\text{-}SiH_4)(PH_3)_4$, **23** $Ru_2H_2[\mu\text{-}H_2Si(OMe)_2]_3(PH_3)_2$. [b] Data for one isomer.

