Inorganica Chimica Acta, 198–200 (1992) 763–769

New silanediyl (silylene) complexes of ruthenium(0)

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Abstract

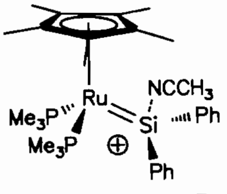
The ruthenium(0)–silanediyl complexes $(t\text{-BuO})_2(\text{HMPA})\text{Si}{=}\text{Ru(CO)}_4$ (**6**), $\text{Me}_2(\text{HMPA})\text{Si}{=}\text{Ru(CO)}_4$ (**7**), $\text{Cl}_2(\text{HMPA})\text{Si}{=}\text{Ru(CO)}_4$ (**8**), $(\text{C}_6\text{H}_5)_2(\text{HMPA})\text{Si}{=}\text{Ru(CO)}_4$ (**9**) and $\text{HCl(HMPA)Si}{=}\text{Ru(CO)}_4$ (**10**) have been obtained from chlorosilanes and carbonylruthenate and characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si (INEPT)NMR and IR spectroscopy. VT ^{1}H NMR spectra in the range 22.0–100.1 °C show a rigid coordination of the HMPA donor to silicon in all cases. The rotation of the metal silicon bond is unrestricted down to −95.0 °C for **6**. Furthermore, the TBP framework of the ruthenium complexes is fluxional (Berry pseudorotation). A comparison of the force constants ν(CO) of the CO stretching vibration *trans* to silicon allows the deduction of the donor capacity of the coordinated silanediyl ligands according to the sequence $[(t\text{-BuO})_2(\text{HMPA})\text{Si}] > [\text{Me}_2(\text{HMPA})\text{Si}] > [\text{Cl}_2(\text{HMPA})\text{Si}]$. This gradation correlates with the net charge densities at silicon calculated for the free silanediyls $[(t\text{-BuO})_2\text{Si}] > [\text{Me}_2\text{Si}] > [\text{Cl}_2\text{Si}]$. A single crystal X-ray structure determination for **6** shows a Ru–Si bond distance of 2.414(1) Å and a partial covalent HMPA(O3)–Si donor bond of 1.735(3) Å (Si–O1 1.641(3), Si–O2 1.634(3) Å, $\Sigma = 342.2°$). A force field calculation for **6** reproduces the conformer found in the crystal as the global minimum of energy ($E_{\text{tot}} = 26.0$ kcal mol^{-1}).

Introduction

The organometallic chemistry of silicon has experienced decisive new impulses from the introduction of low valent silicon ligands [1]. Silanediyl coordination compounds, for instance, were so far known only as reactive intermediates of a variety of (catalytic) silanediyl transfer reactions [2] such as the Pannell rearrangement [3] or Si–Si bond formation reactions by Speier catalyst [4] or metal catalyzed crosslinking reactions of polysilanes [5]. With the recently introduced base stabilized silanediyl complexes a promising basis of stable model compounds has been made available which allows a broad investigation of the chemistry of coordinated silanediyl ligands.

Besides silanediyl coordination compounds [6] a large variety of further, hitherto unknown complexes has been isolated recently such as cyclic bissilanediyl complexes [7], base stabilized metalasilaallenes with a formally zerovalent silicon atom [8], or cationic silanetriyl complexes [9]. A common feature of all complexes is the coordination of an additional base to the silicon atom ($CN = 4$) with extension of the coordination sphere to a distorted tetrahedron.

'Electron rich' transition metal fragments of Ru or Os are particularly appropriate for the fixation of highly electrophilic silanediyl ligands. Some rare examples of cationic silanediyl coordination compounds have been described recently by Tilley and co-workers [10]. However, the synthetic access by silyl exchange reactions and chloride abstraction to the compounds mentioned is relatively complex. The acetonitrile adduct **1a** has been characterized by a single crystal X-ray structure analysis; the data are compiled in Table 1.



1a

A further interesting example has been provided with the THF adduct of dimethylsilanediyltetraphenylporphyrin osmium(0) (**2**) introduced recently by Woo *et al.* [12a]. Attempts to remove THF in high vacuum led to decomposition of the compound [12b].

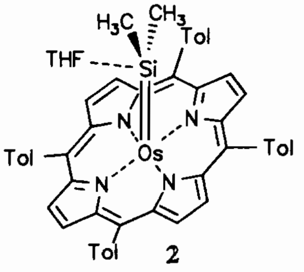


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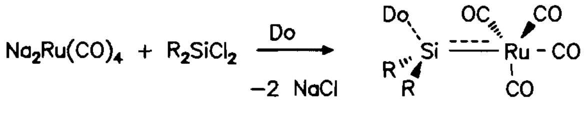
TABLE 1. Comparison of selected structural parameters of silyl and silanediyl complexes of ruthenium(0) and ruthenium(II)

Compound	Ru–Si (Å)	Do–Si (Å)	Σ^c
Ru(II) compounds[a]			
$[Cp^*(Me_3P)_2Ru{=}Si(CH_3CN)Ph_2]^+BPh_4^-$ (**1a**)	2.328(2)	1.923(8)	351.6
$[Cp^*(Me_3P)_2Ru{=}Si(OTf)Ph_2]$ (**1b**)	2.349(2)	1.853(5)	340.6
$Cp^*(Me_3P)_2Ru{-}SiHPh_2$ (**3**)	2.387(1)		342.3
$Cp^*(Me_3P)_2Ru{-}SiClPh_2$ (**4**)			
$C_5H_5(iPr)_3P\overline{RuH(CH_2Si}Ph_2)$ (**5**)	2.382(4)		
	2.365(5)		
Ru(0) complexes[b]			
$(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (**6**)	2.414(1)	1.731(2)	342.2

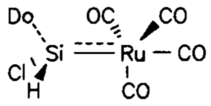
[a] Ref. 11. [b] This work. [c] Sum of bond angles at Si.

Our synthetic method allows an effective access to a variety of neutral (base stabilized) silanediyl complexes in a one step procedure. The silanediyl coordination compounds **6**, **7**, **8**, **9** and $HCl(HMPA)Si{=}Ru(CO)_4$ (**10**) are obtained as HMPA adducts by reaction of disodiumtetracarbonylrhutenate with the respective chlorosilanes (eqn. (1)).



(1)

R=t–BuO **6**
$R=CH_3$ **7**
R=Cl **8**
$R=C_6H_5$ **9**



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Results and discussion

Spectroscopic investigations

The structures of the compounds **6**, **7**, **8** and **9** and the coordination mode of the donor HMPA in particular can clearly be assigned on the basis of the spectroscopic data.

With respect to the base coordination, complexes **6**, **7**, **8** and **9** are surprisingly distinguished from the cationic complex **1a** for which a fast exchange of the donor CH_3CN has been described above −30 °C (coalescence temperature). Temperature variable ^1H NMR spectra in d_8-toluene in the temperature range 22.0–100.1 °C for **6**, **7**, **8** and **9** give no indication for an exchange process of the coordinated HMPA.

Besides exchange phenomena of the donor, the molecular dynamics of the complexes are of interest. VT ^1H NMR spectra of **6** show an unhindered rotation of the metal silicon bond down to −95 °C. Similar to carbene complexes, no rotational barrier of the M=Si double bond is to be expected for the silanediyl compounds **6**, **7**, **8** and **9** on the basis of electronic effects; this effect is due to orthogonal e orbitals (d_{xz}, d_{xy}) at the metal available for metal–silicon π-bonding in base free complexes $R_2Si{=}Ru(CO)_4$. This description can, slightly modified, also be applied to the donor adducts **6**, **7**, **8** and **9**. Furthermore, these findings are also in accordance with observations made for analogous Cr d^6 and Fe d^8 complexes [6a].

In particular ^{29}Si NMR spectroscopy has proved the most reliable method for the diagnosis of the coordination geometry and bonding mode at silicon. The spectroscopic data of silanediyl coordination compounds fall into a shift range between −10 and 150 ppm; with the latter ones typical for base free complexes. Most of the ^{29}Si NMR spectra have been acquired by a classical procedure with broad band decoupling and applying small pulse angles of *c*. 10° to reduce the pulse delay times. Problems arising from Overhauser effects can be overcome in the case of $Me_2(HMPA)Si{=}Ru(CO)_4$ (**7**) by use of DEPT- or INEPT-pulse sequence methods with the parameters $^2J(^1H^{29}Si)=7.2$ Hz, $n=3$, $\tau=\frac{1}{4}J=34.7$ ms; $\Delta_{opt}=(1/\pi J)\arcsin n^{-1/2}=27.2$ ms for a $Si(CH_3)_2$ unit [13]. The observed ^{29}Si NMR chemical shifts show a complex (square) correlation between chemical shift and overall electronegativity at the silicon atom due to the superposition of paramagnetic and diamagnetic shift influences. Therefore, particular shift differences (R_2SiCl_2 versus $R_2(HMPA)Si{=}ML_n$) are of diagnostic value (Table 2). Altogether the ^{29}Si NMR shift data can be considered as a valuable tool for the structure assignment in silanediyl complexes. An analysis of the ν(CO) stretching frequency of the carbonyl located in *trans* position to the silanediyl ligand allows a qualitative assignment of he σ-donor/π-acceptor capacity of the silanediyl ligand. The IR spectra of the TBP $LM(CO)_4$ complexes with an apical silanediyl ligand (C_{3v} sym-

TABLE 2. ^{29}Si NMR data (ppm) for silanediyl complexes of Ru, Fe and Cr $R_2(HMPA)Si{=}M(CO)_n$ (R = t-BuO, CH_3, Cl; M = Fe, Ru, $n = 4$; M = Cr, $n = 5$) and of Ru(II)–silanediyl complexes

Compound	Silane δ	Ru complex δ ($\Delta\delta$)	Fe complex [12] δ ($\Delta\delta$)	Cr complex δ ($\Delta\delta$)
Cl_2SiMe_2	32.0	79.0 (47.0)	92.3 (60.3)	101.4 (69.4)
Cl_4Si	−18.5	33.2 (51.7)	49.7 (68.2)	55.0 (73.5)
$Cl_2Si(t\text{-}BuO)_2$	−72.2	−5.3 (66.9)	7.1 (79.3)	12.7 (84.9)
Compound		δ (ppm) [10a]		
$[Cp^*(Me_3P)_2Ru{=}Si(CH_3CN)Ph_2]^+BPh_4^-$		95.75		
$[Cp^*(Me_3P)_2Ru{=}Si(OTf)Ph_2]$		112.39		
$[Cp^*(Me_3P)_2Ru{=}Si(STol\text{-}p)_2]^+BPh_4^-$		259.4		
$Cp^*(Me_3P)_2Ru{-}SiHPh_2$				
$Cp^*(Me_3P)_2Ru{-}SiPh_2Cl$		74.07		

metry) show a typical pattern of the ν(CO) frequencies of the type A_1 and E. A comparison of the force constants k_{CO} (approximation as harmonic oscillator)* allows the deduction of the donor capacity of the silanediyl ligands in the sequence $(t\text{-}BuO)_2(HMPA)Si > Me_2(HMPA)Si > Cl_2(HMPA)Si$. This gradation correlates with the electron densities at silicon of the free silanediyls [R_2Si] obtained by MNDO calculations (Tables 3 and 4)** and can be interpreted in the sense of increasing electrophilicity and decreasing nucleophilicity, respectively of the silanediyls in the above given sequence. The high donor capacity of the di-t-butoxysilanediyl ($(t\text{-}BuO)_2Si \cdot HMPA$) ligand has also been deduced from ^{57}Fe Mössbauer data ($IS = -0.477$ mm s^{-1} [6g]) for the coordination compound $(t\text{-}BuO)_2(HMPA)Si{=}Fe(CO)_4$ (**11**).

TABLE 3. IR spectra: frequency comparison of selected ν(CO) stretching vibrations (cm^{-1}) and force constants (Nm^{-1}) for complexes **6** and **11** and related metal carbonyls

Compound	Ru	Fe
$(t\text{-}BuO)_2(HMPA)Si{=}M(CO)_4$	2022(1651)	2005(1623)
	1946(1529)	1920(1509)
	1898(1455)	1883(1432)
$M(CO)_5$	2035(1672)	2034(1670)
	1999(1614)	2013(1636)

TABLE 4. MNDO calculations of the silanediyls [$Si(OMe)_2$], [$SiMe_2$] and [$SiCl_2$]

	$Si(OMe)_2$	$SiMe_2$	$SiCl_2$
Heat of formation (kcal/mol)	−127.5	30.8	−46.3
Ionization potential (eV)	9.03	7.50	9.83
Dipole moment (Db)	0.27	0.73	4.18
Net charge Si	1.07	0.73	1.16
Bond distance Si–R	1.63	1.80	2.09
Bond angle R–Si–R (°)	102.4	105.9	105.5

Complex $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (**6**) has also been characterized by a single crystal X-ray structure determination (Tables 5 and 6, Fig. 1). The Ru–Si bond distance of 2.414(1) Å is relatively short, see Table 1 for comparison. The silicon atom shows a distorted tetrahedral coordination sphere with Si–O1 1.641(3) and Si–O2 1.634(3) Å for the two covalent Si–O bonds and 1.735(3) for the donor contact (O3–Si (1.730(3) Å in $(t\text{-}BuO)_2(HMPA)Si{=}Fe(CO)_4$ (**11**)). The two bond angles Ru–Si–O1 (116.8(1)°) and Ru–Si–O2 (121.3(1)°) are still relatively close to 120°, whereas the angle O1–Si–O2 of 104.1(1)° is considerably smaller. MNDO calculations for the 'free' silanediyl [$(MeO)_2Si$] give 102.4° for the angle R–Si–R. The coordination geometry of the silanediyl ligand obviously is only marginally affected upon coordination to the metal (and additional fixation of a donor). In the TBP–Ru d^8 complexes the silanediyl ligand occupies an apical coordination site at the TBP coordination polyhedron due to its higher σ-donor capacity compared to CO. Accordingly, the

TABLE 5. Important bond lengths (Å) and bond angles (°) for $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (**6**)

Ru–Si	2.414(1)	Si–O1	1.641(3)
Si–O2	1.634(3)	Si–O3	1.735(3)
Ru–C1	1.915(5)	Ru–C2	1.924(6)
Ru–C3	1.902(6)	Ru–C4	1.943(6)
C1–O11	1.141(5)	C2–O21	1.142(6)
C3–O31	1.145(6)	C4–O41	1.146(6)
O1–C11	1.445(5)	O2–C12	1.449(5)
O3–P	1.521(3)		
Ru–Si–O1	116.8(1)	Ru–Si–O2	121.3(1)
O1–Si–O2	104.1(1)	Ru–Si–O3	111.9(1)
O1–Si–O3	98.0(1)	O2–Si–O3	101.4(2)
Si–O3–P	143.7(2)		

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*Approximation of the ν(CO) stretching vibration by a harmonic oscillator is common and because of the large mass differences metal–carbon subject to only a small error.

**MNDO calculations were performed with the program QCMPO 17; for details see ref. 14.

TABLE 6. Fractional atomic coordinates and equivalent isotropic displacement parameters for **6** with standard deviations in brackets

Atom	*x/a*	*y/b*	*z/c*	U_{eq}^{a}
Ru	0.08180(4)	0.12964(2)	0.33464(2)	0.034
C1	0.2637(5)	0.1425(3)	0.3006(3)	0.041
C2	−0.0078(6)	0.0422(3)	0.2982(3)	0.049
C3	−0.0207(6)	0.2088(4)	0.3781(4)	0.060
C4	0.1259(6)	0.0942(3)	0.4568(4)	0.059
O11	0.3725(3)	0.1494(2)	0.2809(3)	0.055
O21	−0.597(5)	−0.0099(2)	0.2761(3)	0.074
O31	−0.0808(6)	0.2573(3)	0.4036(3)	0.086
O41	0.1557(5)	0.0743(3)	0.5287(3)	0.081
Si	0.0349(1)	0.17571(6)	0.18259(8)	0.026
O1	0.1509(3)	0.1650(2)	0.1052(2)	0.028
O2	−0.1026(3)	0.1549(2)	0.1282(2)	0.033
O3	0.0284(3)	0.2694(2)	0.1810(2)	0.036
C11	0.1803(4)	0.1053(2)	0.0445(3)	0.030
C111	0.1200(5)	0.1222(3)	−0.0486(3)	0.046
C112	0.1277(5)	0.0344(2)	0.0821(3)	0.040
C113	0.3304(4)	0.1021(3)	0.0393(3)	0.040
C12	−0.2449(4)	0.1617(3)	0.1396(4)	0.042
C121	−0.289(1)	0.2215(6)	0.0718(7)	0.048
C122	−0.281(1)	0.1787(6)	0.2382(7)	0.047
C123	−0.302(1)	0.0875(6)	0.1092(8)	0.061
C124	−0.299(1)	0.1722(7)	0.0433(9)	0.078
C125	−0.278(1)	0.2247(8)	0.207(1)	0.081
C126	−0.289(1)	0.0908(8)	0.184(1)	0.082
P	0.1096(1)	0.33717(6)	0.16269(8)	0.033
N1	0.2609(4)	0.3377(2)	0.1974(3)	0.044
N2	0.1176(4)	0.3486(2)	0.0528(3)	0.047
N3	0.0347(4)	0.3999(2)	0.2208(3)	0.046
C1N1	0.2927(6)	0.3479(4)	0.2943(4)	0.069
C1N2	0.3680(5)	0.3059(3)	0.1446(4)	0.063
C2N1	0.1952(7)	0.4081(4)	0.0123(4)	0.076
C2N2	0.0236(8)	0.3184(4)	−0.0100(4)	0.072
C3N1	0.0862(7)	0.4734(3)	0.2202(5)	0.076
C3N2	−0.1036(7)	0.3959(3)	0.2482(6)	0.081

$^a U_{eq} = U_1 U_2 U_3^{1/3}$; U_1, U_2, U_3 are the eigen values of the U_{ij} matrix.

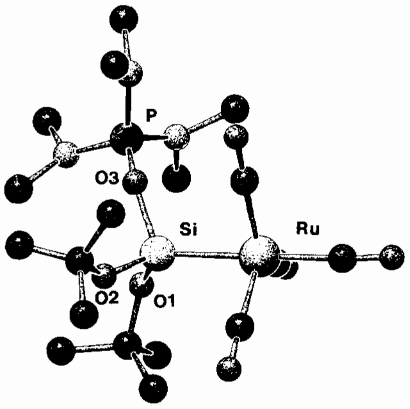

Fig. 1. SCHAKAL view of **6**, hydrogens omitted for clarity.

Ru–C4 bond of the carbonyl *trans* to the silanediyl ligand is somewhat elongated to 1.943(6) Å, compared to the equatorial COs of 1.915(5), 1.924(6) and 1.902(6) Å, with an average bond distance for the equatorial COs of 1.914 Å.

All further bond distances are within the range of expectation. Known Ru–Si bond distances of related compounds are listed in Table 1 for the purpose of comparison. The shortest metal silicon bond lengths have been found for $[Cp^*(Me_3P)_2Ru{=}Si(CH_3CN)Ph_2]^+BPh_4^-$ (**1a**) (2.328(2)) and $[Cp^*(Me_3P)_2Ru{=}Si(OTf)Ph_2]$ (**1b**) (2.349(2) Å); for these compounds a significant degree of metal–silicon multiple bonding is assumed. Surprisingly, in the cationic Ru(II)–silanediyl complex (**1a**) the Ru–Si bond distance is only 0.059 Å shorter than in the neutral silyl hydride $Cp^*(Me_3P)_2RuH{-}SiHPh_2$ (**3**) (2.387(1) Å). Further reference values are available from the silaethene complex **5** with Ru–Si 2.382(4)/2.365(5) Å. Taking the different oxidation states and charges in **1a** and **6** into account, a considerable degree of multiple bonding can be deduced also for **6** (the Ru–Si bond distance in $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (**6**) of 2.414(1) Å is only 0.086 Å longer than in **1a**).

Molecular modeling

The complex $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (**6**) has a typical conformation in the crystal which is similar to that found for the complexes $(t\text{-}BuO)_2(HMPA)Si{=}Fe(CO)_4$ (**11**), $(t\text{-}BuS)_2(HMPA)Si{=}Fe(CO)_4$ (**12**) and $(t\text{-}BuO)_2(HMPA)Si{=}Cr(CO)_5$ (**13**). The three 'organic' substituents at silicon form a typical paddle wheel array reducing the C_s symmetric form found in solution to C_1 symmetry (Fig. 2).

This conformation in the crystal can be reproduced by a force field calculation as a global minimum of

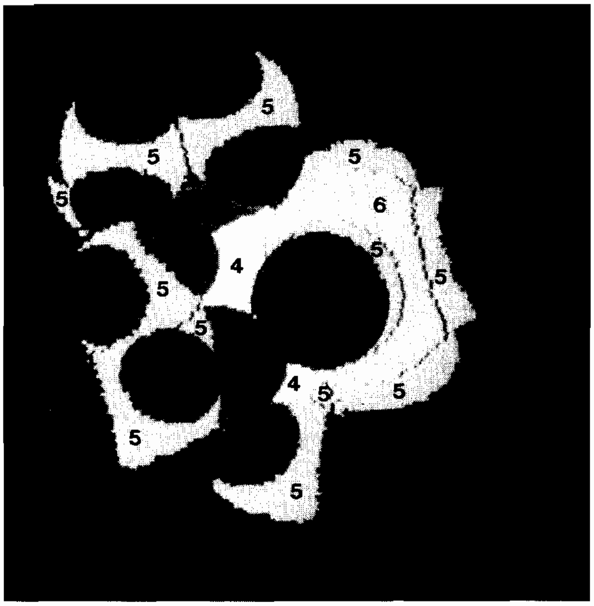

Fig. 2. van der Waals radii of the energetically most favoured conformation of **6** obtained by force field calculation. Colour code: 1, turquoise; 2, blue; 3, red; 4, yellow; 5, light brown; 6, pink.

TABLE 7. Force field calculation (kcal mol^{-1}) for **6**[a]

E_{tot}	26.0
E_{str}	7.6
E_{ang}	17.8
E_{tor}	13.7
E_{vdw}	−13.1

[a] Calculated distances Ru–Si 2.416 Å, Si–O3 1.714 Å and bond angle O1–Si–O2 103.3°.

energy which is obviously caused by steric interactions of the ligands. The total energy E_{tot} of the molecule is obtained as the sum of contributions from stretching E_{str} and bending E_{ang} vibrations, torsional movements E_{tor} and attractive as weell as repulsive van der Waals interactions E_{vdw}: $E_{tot}=E_{str}+E_{ang}+E_{tor}+E_{vdw}$. A detailed analysis of the calculated energy distribution shows a significant contribution to the total energy of the molecule by attractive van der Waals forces (Table 7). According to these results, packing forces in the crystal seem to have only a small effect on the molecular conformation of **6**.

Reactive silanediyl complexes

The stabilizing (heavy atom) effect of ruthenium can be utilized for the fixation of the extremely labile chlorosilanediyl ligand [Cl–Si–H]. The synthesis of the respective HMPA adduct **10** requires reaction of chlorosilane with $Na_2Ru(CO)_4$ in THF at −60 °C. The obtained coordination compound **10** is thermally unstable and decomposes with $t_{1/2}=12$ h by loss of the silanediyl ligand. However, characterization of $HCl(HMPA)Si{=}Ru(CO)_4$ (**10**) with NMR spectroscopy is possible (^{29}Si NMR, d_8-THF, 22 °C, $\delta=56.2$, dd, $^{1}J(^{1}H^{29}Si)=218$ Hz, see 'Experimental'). Further investigations, particularly toward the application of **10** as a building block for further reactions are under way.

Experimental

General comments

All experiments were performed in an atmosphere of purified argon; solvents were dried rigorously over NaK-alloy, P_4O_{10}, etc. The residual water content was below 3 ppm (K. Fischer titration) in all cases.

NMR spectra were recorded on the spectrometers Jeol GX 270 and GX 400, IR spectra on a FT-IR-spectrometer Nicolet 5 DX and mass spectra were obtained on the instruments MAT 311 A (EI) and MAT 90 (CI).

Syntheses

Di-t-butoxysilanediylruthenium(0)tetracarbonyl·HMPA (t-BuO)$_2$(HMPA)Si=Ru(CO)$_4$ (6)

A suspension of 3.08 g (11.9 mmol) of $Na_2Ru(CO)_4$ in 200 ml of THF was treated with 15–20 ml of HMPA until a clear brown solution was obtained and then cooled down to −50 °C. 2.6 ml (11.9 mmol) of $(t\text{-}BuO)_2SiCl_2$ were added and the mixture was allowed to warm to room temperature and stirred for a further 5 h. Precipitated NaCl was allowed to settle and the formed clear solution was transferred into another flask through a steel cannula. After removal of all volatile components in the vacuum, residual HMPA was pumped off at 10^{-4} mbar, 50 °C, 7 h. The obtained viscous, glassy residue was dissolved in 20 ml of THF and layered carefully with 20 ml of pentane. **6** crystallized as colourless needles. Yield 0.97 g (21%), m.p. 148 °C (dec.). ^{1}H NMR (C_6D_6, 22 °C): $\delta=1.57$ (s, 18H, CH_3), 2.25 (d, $^{3}J(^{31}P^{1}H)=9.8$ Hz, 18H, HMPA). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 23 °C): $\delta=32.3$, 73.3 (s, t-butyl), 36.6 (d, $^{2}J(^{31}P^{13}C)=5.5$ Hz, HMPA), 210.9 (s, CO). ^{29}Si NMR (C_6D_6, 22 °C): $\delta=-5.3$ (d, $^{2}J(^{31}P^{29}Si)=25.7$ Hz). IR (KBr, cm^{-1}): 2022(m), 1964(s), 1898(ss), ν(CO). IR (THF, cm^{-1}): 2024(m), 1963(m), 1944(s), 1910(ss), 1900(ss), ν(CO). MS (EI): m/z (%) = 483 ($M^{+}-3CO$) (5.4). *Anal.* Calc. for $C_{18}H_{36}N_3O_5PSiRu$ (566.76): C, 38.16; H, 3.20. Found: C, 38.02; H, 3.25%.

Dimethylsilanediylruthenium(0)tetracarbonyl·HMPA, Me$_2$(HMPA)Si=Ru(CO)$_4$ (7)

2.25 g (8.86 mmol) of $Na_2Ru(CO)_4$ dissolved in a mixture of 150 ml of THF and 10 ml of HMPA were treated with 1.05 ml (8.68 mmol) of Me_2SiCl_2. The reaction mixture was worked up as described for **6**. **7** crystallized from THF/pentane as colourless rodlets. ^{1}H NMR (C_6D_6, 22°C): $\delta=0.89$ (s, CH_3), 2.39 (d, $^{3}J(^{31}P^{1}H)=8.2$, HMPA). ^{13}C NMR (C_6D_6, 23 °C): $\delta=12.4$ (q, $^{1}J(^{1}H^{13}C)=118.6$ Hz, CH_3), 36.6 (q, $^{1}J(^{1}H^{13}C)=136.5$ Hz, HMPA), 210.5 (s, CO). ^{29}Si NMR (C_6D_6, 22 °C): $\delta=79.0$ (d, $^{2}J(^{31}P^{29}Si)=23.0$ Hz. IR (THF): 1894(s), 1899(s) 1937(m) 1995(m) 2018(s).

Dichlorosilanediylruthenium(0)tetracarbonyl·HMPA, Cl$_2$(HMPA)Si=Ru(CO)$_4$ (8)

1.12 ml (9.77 mmol) of $Na_2Ru(CO)_4$ dissolved in 200 ml of THF and 15 ml of HMPA were reacted with 2.53 (9.77 mmol) of $SiCl_4$. The work-up procedure was done as described above. **8** was obtained as a brown oily product in 43% yield. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C): $\delta=36.5$ (q, $^{1}J(^{1}H^{13}C)=135.5$ Hz, HMPA), 211.6 (s, CO). ^{29}Si NMR (C_6D_6, 22 °C): $\delta=33.2$ (d, $^{2}J(^{31}P^{29}Si)=32.2$ Hz).

Diphenylsilanediylruthenium(0)tetracarbonyl·HMPA, $(C_6H_5)_2(HMPA)Si{=}Ru(CO)_4$ (9)

The compound was synthesized by the same procedure as described above for **6**, yield 57%. ^{1}H NMR (C_6D_6, 22 °C): $\delta = 2.36$ (d, $^3J(^{31}P^1H) = 9.2$ Hz, 18H, HMPT), 7.12–8.06 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): $\delta = 36.3$ (d, $^2J(^{31}P^{13}C) = 9.2$ Hz), 127.5 (s, C_6H_5-*o*), 128.3 (s, C_6H_5-*p*), 135.1 (s, C_6H_5-*m*), 145.3 (s, C_6H_5-*i*), 209.6 (s, CO). IR (THF): 1896(s), 1906(s), 1944(m), 1998(m), 2022(s). ^{29}Si NMR (C_6D_6, 23 °C): $\delta = 73.9$ (d, $^2J(^{31}P^{29}Si) = 21.1$ Hz).

Chlorosilanediylruthenium(0)tetracarbonyl·HMPA, $HCl(HMPA)Si{=}Ru(CO)_4$ (10)

To a solution of 3.39 g (0.013 mmol) of $Na_2Ru(CO)_4$ in 100 ml of THF and 10 ml of HMPA, 1.32 ml (0.013 mmol) of $HSiCl_3$ were added at -40 °C. The reaction mixture was stirred at room temperature for further 2 h. Precipitated NaCl was removed by filtration and the volatile components were pumped off in the vacuum. Yield 23%. ^{1}H NMR (d_8-THF, 19 °C): $\delta = 2.57$ (d, $^3J(^{31}P^1H) = 10.0$ Hz, HMPA), 6.63 (s, SiH). ^{29}Si NMR (d_8-THF, 22 °C): $\delta = 56.2$ (dd, $^1J(^1H^{29}Si) = 218.0$ Hz, $^3J(^{31}P^1H) = 23.0$ Hz). IR (Nujol, cm^{-1}): 2361 ν(SiH); 2031, 1953, 1911 ν(CO).

Single crystal X-ray structure analysis of di-t-butyloxysilanediylruthenium(0)tetracarbonyl·HMPA, $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (6)

A single crystal of the dimensions 0.3×0.45×0.5 mm was mounted into a glass capillary on a CAD 4 diffractometer. Intensities $-h \rightarrow h$, $0 \rightarrow k$, $0 \rightarrow l$ were measured for a monoclinic cell, space group $P2_1/n$ (No. 14) with $a = 10.064(2)$, $b = 18.500(2)$, $c = 14.551(2)$ Å, $\beta = 90.47(1)°$, $V = 2709$ Å^3, Z = 4, $D_{calc} = 1.39$ g/cm^3 at 25 °C (ω-scan, Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator). A total of 5696 independent reflections was collected in the range of $2 < \theta < 26°$, of which 5502 reflections with $F_0 > 4\sigma(F_0)$ were used for structure refinement and absorption correction. The positional parameters of the ruthenium atom were calculated from the Patterson map (SHELXS-86) [15]. A difference Fourier map (SHELX-76) [16] revealed the positions of the remaining non-hydrogen atoms. The three methyl groups of the second t-butoxy substituents were found to be disordered over two distinct positions (refined isotropically, site occupance 0.5). Refinement of the remaining non-hydrogen atoms was done anisotropically by full matrix least-squares methods, hydrogen atoms were included in calculated positions. Final residuals are $R = 0.0403$ and $R_w = 0.0398$. Selected interatomic bond distances and angles are listed in Table 5, atomic coordinates with isotropic displacement parameters in Table 6. See also 'Supplementary material'.

MNDO calculation of the silanediyls $[Si(OMe)_2]$, $[SiMe_2]$ and $[SiCl_2]$

Calculations were performed with a semiempirical MNDO method with the program QCPE 017. The SCF-iterations converged after 10–15 cycles. For details see ref. 6g.

Force field calculation for di-t-butoxysilanediylruthenium(0)tetracarbonyl, $(t\text{-}BuO)_2(HMPA)Si{=}Ru(CO)_4$ (6)

The force field was optimized with the ALCHEMY-minimizer program $E_{tot} = E_{str} + E_{ang} + E_{tor} + E_{vdw}$ with $E_{str} = \Sigma_{i=1}^{N} k^{d}{}_{i}/2(d_i - d^0{}_i)^2$, $d^0{}_{RuSi} = 2.400$ Å, $k_{RuSi} = 1500$ kcal/mol Å^2; $E_{ang} = \Sigma_{i=1}^{N} k^{\theta}{}_{i}/2(\theta_i - \theta^0{}_j)^2$, $\theta^0{}_{RuSiO} = 115°$, $k^{\theta}{}_{RuSiO} = 0.03$ kcal/mol°^{2}; $E_{tor} = \Sigma_{i=1}^{N} k_i/2(1 + \text{sign}(\text{per}_i) * \cos(|\text{per}_i| * (\omega_i))$, $\omega_{RuSi**} = 0.1$ kcal/mol°^{2}; $E_{vdw} = \Sigma_{i=1}^{N}(\Sigma_{j>i} E_{ij}[1.0/a^{12}{}_{ij} - 2.0/a^{6}{}_{ij}])$, $E_{RuSi} = 0.200$ kcal/mol, $a_{Ru} = 3.100$ Å. All further parameters were used as given in the program.

Supplementary material

Calculated and observed structure factor amplitudes together with a complete list of atomic coordinates and thermal parameters have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein Leopoldshafen 2, FRG and are available on request quoting the deposition number CSD 56225, the names of the authors and the journal citation.

Acknowledgements

This work has been supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. We are indebted to Professor H. Schmidbaur for generous support of our investigations. We are also grateful to Mr J. Riede for measurement of the crystallographic data set and Dr M. Heiss for an introduction to the MNDO program.

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