

Transition Metal Complexes of Silylenes, Silenes, Disilenes, and Related Species

Paul D. Lickiss

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

1 Introduction

Carbene, carbyne, and alkene complexes are some of the commonest organo-transition metal compounds and their structures and chemistry are well studied, but until quite recently no analogous silicon compounds containing, for example, silylene, silylyne, silene, or disilene ligands ($R_2Si:$, $RSi:$, $R_2C=SiR_2$, and $R_2Si=SiR_2$, respectively) had been isolated. There are many synthetic routes to both carbene and alkene complexes but they often require starting materials for which there are no silicon-containing analogues. For example, carbene complexes can be prepared by the addition of alkyllithium reagents to metal carbonyl complexes, by addition of alcohols to isocyanide complexes, and by use of electron-rich olefins, while none of the multiply bonded silicon analogues with, for example, SiO or $Si\equiv NR$ as ligands are available. Although many unstable free silylenes have been generated, none so far seem to have been trapped in a manner similar to that for example of $H_2C:$ on a transition metal centre. Similarly the synthesis of most alkene complexes requires a free alkene as a starting material and although free disilenes and silenes can be isolated they are usually too bulky to react readily with a suitable transition metal precursor.

The techniques used to characterize silicon-containing complexes are similar to those used for their carbon analogues. Thus ^{29}Si NMR spectroscopy, from which chemical shifts and coupling constants give an indication of the hybridization of the silicon, and X -ray crystallography, where short bond lengths to silicon and sp^2 -like angles at silicon also indicate double bond character, have both been used extensively. Reviews of the now well established chemistry of uncoordinated silylenes, silenes, and disilenes as well as that of the vast array of transition metal silyl complexes $M-SiR_3$ can be found in reference 1.

2 Complexes Containing Silylenes and Silylynes

Although the chemistry of silylene complexes of transition metals is more advanced than that of either silene or disilene complexes, many more compounds containing a wider variety of metals and different groups on the silicon need to be prepared before clear trends in structural features and spectroscopic properties can be observed. Complexes in which a silylene acts as a bridging group between two transition metal atoms have been known for some time (see reference 2 and references therein for a recent discussion of such compounds) but it is only recently that complexes containing terminal silylene ligands have been isolated, and it is these compounds that will be discussed here. In contrast to carbene complexes, almost all of the compounds so

far prepared containing a terminal silylene ligand are stabilized by coordination of a donor atom such as N or O to the silicon. Some of the most recent work, however, has shown that careful choice of substituents on the silicon allows species without such base stabilization to be prepared. As would be expected the $M=Si$ bond is usually somewhat shorter than a related $M-Si$ bond. Several preparative routes such as displacement of good leaving groups from Si in silyl complexes, photochemical rearrangements, and salt eliminations have all been used with success and the compounds will be grouped together roughly according to their means of preparation.

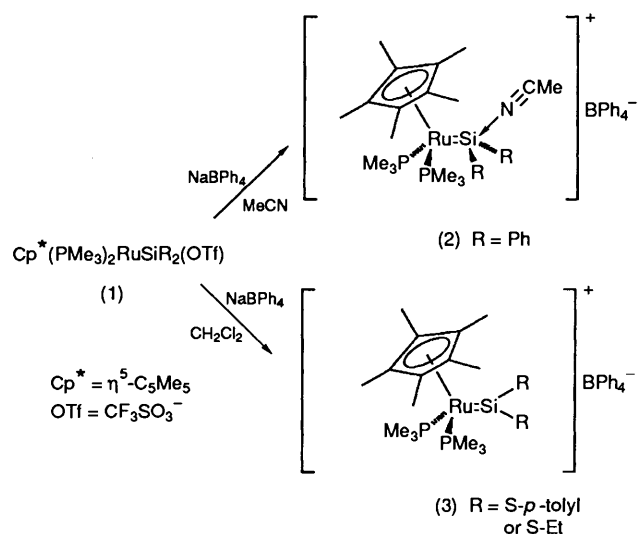
2.1 Displacement of Good Leaving Groups from Si

The X -ray crystal structure of the ruthenium silyl complex (1; $R = Ph$) shows a fairly short $Ru-Si$ distance of 2.349 Å and an exceptionally long $Si-O$ distance of 1.853 Å ($Si-O$ distances are usually 1.63–1.65 Å) which suggests that the compound has some silylene character and that the triflate group is acting to some extent as an anionic donor ligand. Displacement of the triflate group with $NaBPh_4$ in MeCN gives the acetonitrile complex (2). The IR spectrum of (2) shows a $C\equiv N$ stretching frequency of 2395 cm^{-1} (*i.e.* somewhat greater than free MeCN) indicative of considerable electron density donation to the silicon from the MeCN. The X -ray crystal structure of (2) shows a short $Ru-Si$ distance of 2.328 Å ($Ru-Si$ distances normally average about 2.44 Å) and an unusually long $Si\cdots N$ (donor) distance of 1.932 Å ($Si-N$ bond distances are usually about 1.73 Å). The Si to N distance and the bond lengths and angles within the acetonitrile ligand are all consistent with a dative interaction between the MeCN and the silicon rather than the presence of an $Si-N$ sigma bond. The acetonitrile ligand in (2) is labile and exchanges with free MeCN *via* a dissociative process, thus providing evidence for the donor-free silylene complex $[Cp^*(PMe_3)_2Ru=SiPh_2]BPh_4$ – analogues to (3) – in solution.³ Tilley has also used the stabilizing effect of thiolate groups on the silicon to allow the first base-free silylene complexes (3) to be isolated as yellow, crystalline solids.⁴ As would be expected by comparison with carbene complexes the ^{29}Si NMR chemical shifts of (3) are at very low field, a broad signal at room temperature at 250.6 ppm for $R = p$ -tolyl and a broad signal at 264.4 ppm at $-60^\circ C$ for $R = Et$. The base-free complex (3; $R = S$ -*p*-tolyl) readily coordinates MeCN to give a corresponding base-stabilized species ($\delta\ ^{29}Si$, 58.3 ppm).⁴ It would be of great interest to determine the solid state structure of these donor-free complexes in order to compare their structural features with those that do contain donor ligands.

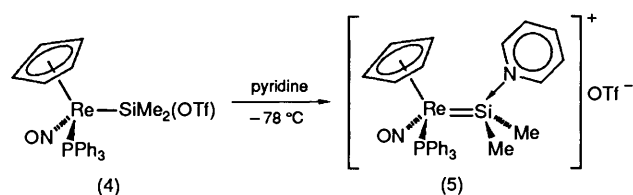
The ruthenium complex (2) reacts with alcohols, ROH , to give alkoxysilanes, $Ph_2SiH(OR)$ ($R = Me$ or Et), and with enolizable ketones, $RC(O)Me$, to give silylenoethers, $Ph_2(H)SiOC(R)=CH_2$ ($R = Me$ or Ph). These reactions apparently proceed *via* dissociative loss of MeCN to give the corresponding base-free complex which then undergoes addition reactions across the $Ru=Si$ double bond; finally, reductive elimination occurs to give the observed products. The base-stabilized complex does not react readily with benzophenone or with Ph_3SiH or Ph_2SiH_2 but gives a mixture of unidentified products when treated with $PhSiH_3$.⁵

The displacement of a triflate group from the ruthenium complex (4) by pyridine, in a manner similar to that for the ruthenium complexes above, affords the base-stabilized com-

Paul Lickiss gained his B.Sc. (1980) and D.Phil. (1983) degrees at the University of Sussex. His D.Phil. was supervised by Professor C. Eaborn, F.R.S. After a postdoctoral year with Professor A. G. Brook at the University of Toronto he returned to Sussex in 1985 as a Royal Society 1983 University Research Fellow and held this fellowship until 1989 when he took up his current position as Lecturer at the University of Salford. His research interests include organometallic chemistry and the use of ultrasound in synthesis.

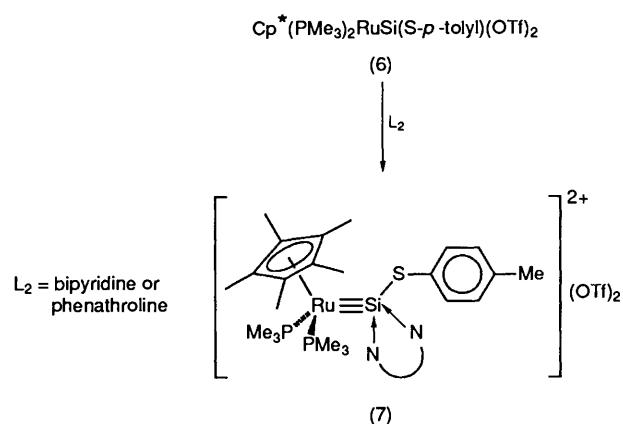


plex (5), as judged by IR spectroscopy which indicates that both triflate and pyridinium ions are present. Also NMR data indicate that the treatment of $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{SiMe}_2\text{Cl})]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with AlCl_3 leads to the diastereotopic SiMe_2 methyl group signals becoming equivalent. This has been interpreted as due to the formation of the base-free silylene complex $[\text{CpRe}(\text{NO})(\text{PPh}_3)=\text{SiMe}_2]^+ \text{AlCl}_4^-$ as an intermediate which can reform the chlorosilyl compound by attack of Cl^- from either face of the $\text{Re}=\text{SiMe}_2$ unit, thus providing a mechanism for methyl group exchange.⁶

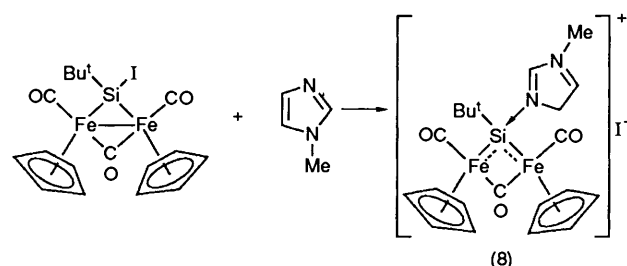


2.1.1 Complexes Containing Silylyne-like Ligands

In an extension to the reactions described above for the preparation of silylene complexes, displacement of two triflate groups from silicon in complex (6) by chelating bases ($\text{L}_2 = \text{bipyridine}$ or phenanthroline) leads to the formation of (7) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in which there is formally a silylyne ligand. For compound (7) ($\text{L} = \text{phenanthroline}$) the ^{29}Si NMR chemical shift, 72.95 ppm, is similar to that of the analogous silylene complex (5) discussed above of 58.3 ppm, the $\text{Si}\cdots\text{N}$ distances are similarly long, and the $\text{Ru}-\text{Si}$ bond length of 2.269(5) Å is short.⁷

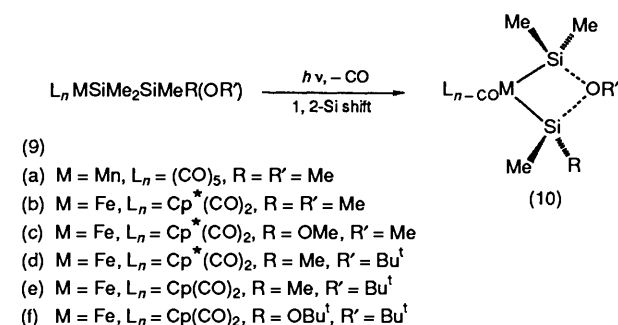


The iron complex (8) containing a silylyne ligand (perhaps better described as a μ_2 -silylydyne ligand) was prepared as a red solid by displacement of iodine from silicon. As for the silylene complexes discussed above there is base stabilization, this time by the strong Lewis base *N*-methylimidazole. The Si to I distance of 5.388 Å is too large for a bonding interaction and the Si to N distance of 1.885 Å is also too long for a normal covalent Si-N bond length. The Si-Fe distance of 2.262(2) Å is slightly shorter than in neutral silylene bridged diiron complexes such as $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu\text{-SiHBU}^t)]$ which has Si-Fe distances of 2.270(1) and 2.272(1) Å. Such a shortening might, however, be expected when comparing a cationic with a neutral species. The FAB mass spectrum of (8) gives a peak for the base free cation $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu_2\text{-SiBU}^t)]^+$ and the ^{29}Si NMR spectrum shows an unusually low field signal at 251.5 ppm, also consistent with the presence of a bridging silylyne (silylydyne) ligand.⁸



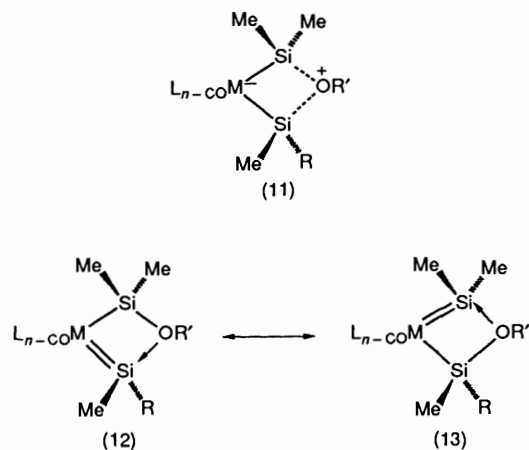
2.2 Photolysis of Metal Silyl Complexes

The photolysis of a range of metal disilanes (9) containing a terminal alkoxy group leads to the loss of CO and formation of the intramolecularly donor-stabilized bis-silylene complexes (10).^{9a,10} The ^{29}Si NMR spectrum of the manganese bis-silylene complex shows a single chemical shift at 115.4 ppm while the *X*-ray crystal structure shows that the compound has short Mn-Si bonds and long $\text{Si}\cdots\text{O}$ distances (see Table 1) all of which is indicative of double bond character. The sum of the C-Si-C and Mn-Si-C angles are 350.3 and 350.9° respectively which also suggests sp^2 character for the silicon and $p\pi-d\pi$ Si to Mn interaction. The methoxy group can readily be exchanged for OCD_3 using excess CD_3OD at room temperature without breaking down the complex, although decomposition does occur after several hours.¹⁰

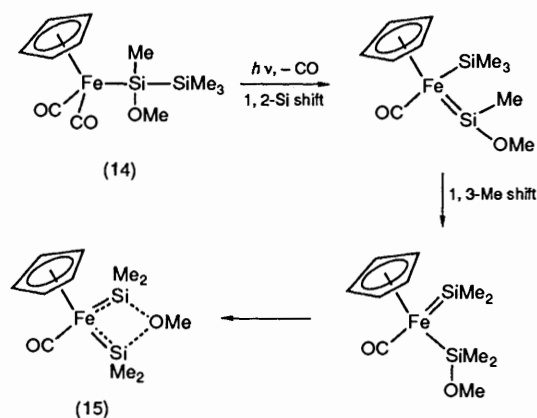


The *X*-ray structure of yellow crystals of the isomer of (10; $\text{M} = \text{Fe}, \text{L}_n\text{-co} = \text{Cp}^*\text{CO}, \text{R} = \text{OMe}, \text{R}' = \text{Me}$) in which the OMe group and the CO group are on the same side of the FeSi_2O ring has similar features to the Mn analogue *i.e.* short Fe-Si distances and long Si-OMe (bridging) distances [average 1.796 Å, *cf.* the Si-OMe (terminal) distance of 1.632 Å]. The complexes are soluble in non-polar solvents suggesting little charge separation [as for example in a canonical form such as (11)] and that the bonding may better be described in classical terms as a mixture of the two resonance structures (12) and (13). The ^{29}Si NMR spectrum of a mixture of the two isomers of (10; $\text{M} = \text{Fe}, \text{L}_n\text{-co} = \text{Cp}^*\text{CO}, \text{R} = \text{OMe}, \text{R}' = \text{Me}$) shows signals at low field (see Table 1), which also suggests that sp^2 silicon atoms are

present.^{9a} Similar rearrangements to give alkoxy-bridged bis(germylene)iron complexes analogous to (10) have recently been reported.^{9b}

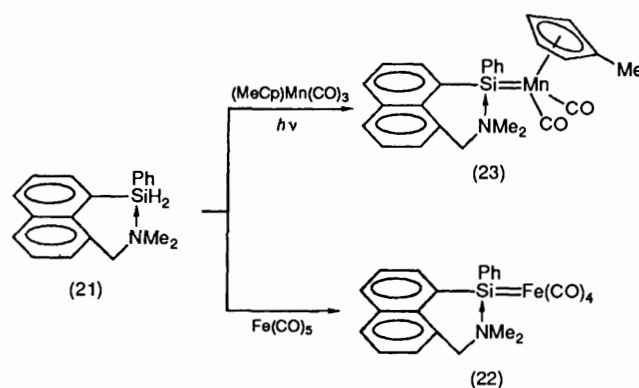


Photolysis of the iron disilane (14) which has only methyl groups on the silicon β to the iron affords the silylene complex (15), apparently *via* a 1,3-methyl migration. The ²⁹Si NMR chemical shift of 123.7 ppm is again at unusually low field.^{9a}

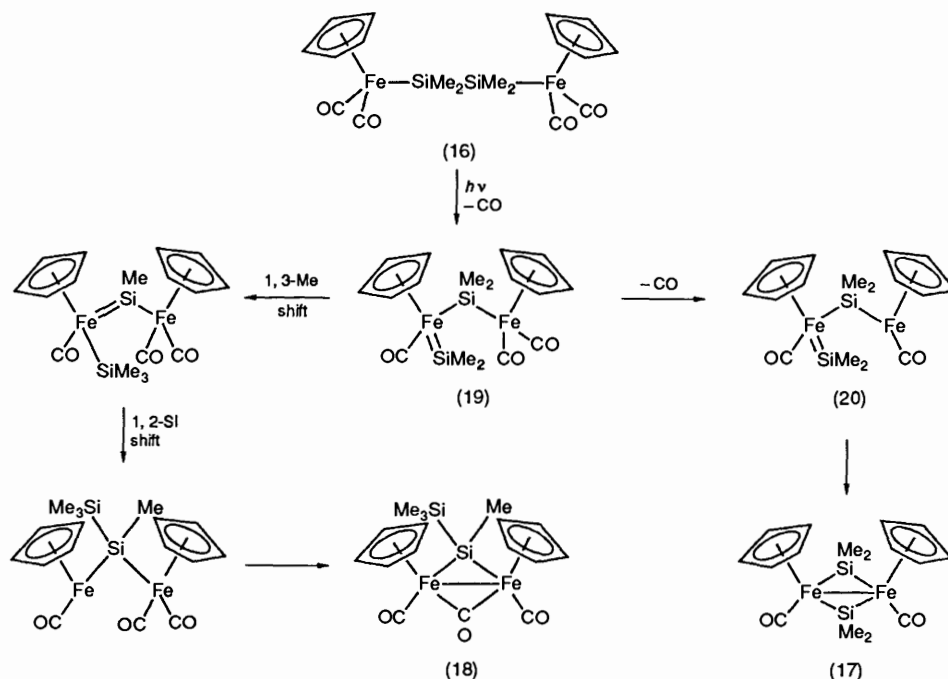


The photolysis of (16) has been studied by two groups.^{11,12} The isomeric silylene bridged iron dimers (17) (all geometrical isomers) and *cis* and *trans* (18) are formed, the latter compounds being formed in increasing amounts as photolysis proceeds. The red-violet isomer of (18) with the Me₃Si and the C₅H₅ rings all *cis* precipitates to give crystals suitable for X-ray crystallography. It has Fe–Si distances of 2.294 and 2.301 Å and the Me₃SiSiMe bridging silicon atoms and those in *cis* and *trans* isomers of (17) have ²⁹Si values at very low field, between about 230 and 245 ppm.¹² The formation of these complexes is thought to proceed *via* the Fe=SiMe₂ containing species (19) which can either lose a second CO molecule to give (20) and then (17) or it can rearrange by a 1,3-Me migration and a 1,2-SiMe₃ migration to give (18).^{11,12}

Silylene complexes stabilized by intramolecular base coordination can also be made by photolysing the five-coordinate SiH₂ compound (21) with metal carbonyls as shown in Scheme 1. The iron and manganese complexes (22) and (23) have ²⁹Si NMR chemical shifts of 101.1 and 124.0 ppm respectively which is indicative of the M=Si interaction. The iron complex does not react with PhC≡CH, 2,3-dimethylbutadiene, methanol, or sulfur but does react readily with moisture to give a cyclic trisiloxane.¹³

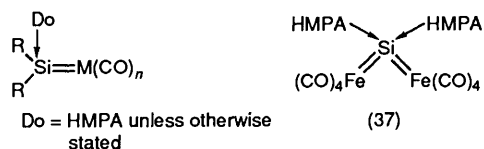


Scheme 1



2.3 Salt Elimination Routes to Silylene Complexes

A conceptually simple way in which an M=Si bond may be formed is from the reaction between a metal dianion and a silicon dihalide with the elimination of two equivalents of a salt. This method does indeed work well although the products again tend to contain a donor ligand coordinated to the unsaturated silicon. The donor-stabilized complexes (24)–(29), (30)–(35), and (36) are isolated as solids from the reactions between $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Cr}(\text{CO})_5]^{2-}$, and $[\text{W}_2(\text{CO})_{10}]^{2-}$ with the corresponding dichlorosilanes R_2SiCl_2 , respectively.^{14–17} Complex (37) arises in a similar manner from the reaction of SiCl_4 with two equivalents of $[\text{Na}_2\text{Fe}(\text{CO})_4]$.¹⁸



- (24) $\text{R} = \text{OBu}^t$, $\text{M} = \text{Fe}$, $n = 4$
 (25) $\text{R} = \text{OBu}^t$, $\text{M} = \text{Fe}$, $n = 4$, $\text{Do} = \text{THF}$
 (26) $\text{R} = \text{SBu}^t$, $\text{M} = \text{Fe}$, $n = 4$
 (27) $\text{R} = \text{SBu}^t$, $\text{M} = \text{Fe}$, $n = 4$, no Do present
 (28) $\text{R} = \text{Me}$, $\text{M} = \text{Fe}$, $n = 4$
 (29) $\text{R} = \text{Cl}$, $\text{M} = \text{Fe}$, $n = 4$
 (30) $\text{R} = \text{Bu}^t\text{O}$, $\text{M} = \text{Cr}$, $n = 5$
 (31) $\text{R} = \text{Me}$, $\text{M} = \text{Cr}$, $n = 5$
 (32) $\text{R} = \text{Cl}$, $\text{M} = \text{Cr}$, $n = 5$
 (33) $\text{R} = \text{OAdam}$, $\text{M} = \text{Cr}$, $n = 5$
 (34) $\text{R} = \text{OCH}_2\text{Bu}^t$, $\text{M} = \text{Cr}$, $n = 5$
 (35) $\text{R} = \text{Ph}_3\text{C}$, $\text{M} = \text{Cr}$, $n = 5$
 (36) $\text{R} = \text{OBu}^t$, $\text{M} = \text{W}$, $n = 5$

The metal to silicon distances in this type of complex are shown in Table 1, and they can again be seen to be relatively short, but unfortunately comparative data for related $\text{M}-\text{SiR}_3$ species are scarce. The $\text{Si}\cdots\text{O}$ (donor, HMPA) distances in these complexes are also significantly longer than usual covalent $\text{Si}-\text{O}$ distances [e.g. 1.610 Å and 1.634 Å for the $\text{Si}-\text{OBu}^t$ in (24)] which is again indicative of a coordination complex and not a sigma $\text{Si}-\text{O}(\text{HMPA})$ bond. The coordination of the HMPA molecule gives a distorted tetrahedral geometry at silicon in (24) and the silylene is in an apical position of the $\text{Fe}(\text{CO})_4$ trigonal bipyramid.¹⁴ In complex (37) the silicon bridges, in an apical position, two trigonal-bipyramidal iron centres. The geometry at the silicon atom in (37) is distorted tetrahedral with an $\text{Fe}-\text{Si}-\text{Fe}$ angle of 122.6° and $\text{Fe}-\text{Si}$ distance of 2.34 Å, *i.e.* somewhat longer than in (24) or (28). Again the $\text{Si}\cdots\text{O}$ distances to donor ligand are unusually long and reflect a ligand to silicon donor interaction and not a σ bond; the silicon may thus be regarded as in a formally zero valent state.¹⁹

The ^{29}Si NMR chemical shift in the iron complex (24) is 7.1 ppm and if HMPA is replaced by THF as donor the resulting complex has a ^{29}Si NMR chemical shift of -9.4 ppm, and the chromium complex (30) has a shift of 12.7 ppm. These values are similar to those for donor adducts of free silenes but are at much higher field than the complexes described above prepared by photolysis; this may be attributed to the change from carbon to oxygen substituents on the silicon. For example it can be seen that substitution of one methyl group for an alkoxy group in compounds of type (10) leads to an upfield shift of approximately 30 ppm (see Table 1). The ^{29}Si chemical shift of the methyl-substituted (28) is +92.4 ppm, *i.e.* similar to the bridged complexes (10) described above.

The chemistry of these silylene complexes has not yet been studied very extensively but iron complexes (24), (26), and (28) and the related chromium complex (30) appear to undergo sequential loss of a carbonyl and silylene ligand under photolysis in the presence of Ph_3P to give $(\text{PPh}_3)_2\text{Fe}(\text{CO})_3$ and $(\text{PPh}_3)_2\text{Cr}(\text{CO})_4$ respectively. In the absence of trapping agents polysilanes are formed but in the presence of 2,3-dimethylbutadiene (a well known silylene trap) silacyclopentenes are formed,

Table 1 Selected structural data and ^{29}Si NMR chemical shifts for silylene and silylyne complexes

Compound	M-Si Distance (Å)	Si \cdots D ^a Distance (Å)	^{29}Si NMR Chemical Shift (ppm)	Ref.
2	2.328	1.932	95.75	3
3, HMPA	—	1.872	58.30	1c
3			250.6 ^b	4
3, R = SEt			264.4 ^c	4
3, R = <i>c</i> -C ₆ H ₁₁			268.7	4
7, R = phenanthroline	2.269	1.91, 1.95	72.95	1c, 7
8	2.262	1.885	251.5	8
10a	2.336	1.784	115.4	10
	2.344	1.795		
10b			125.2	9a
10c	2.207	1.793	93.9, 98.9 ^d	9a
	2.222	1.799	121.1, 127.4	
10d			126.2	9a
10e			122.3	9a
10f			121.6, 89.6	9a
17			243.8, 229.5 ^d	11
18, all- <i>cis</i> isomer	2.294		245.5, 242.7 ^e	11
	2.301		232.1	
22			101.1	13
23			124.0	13
24	2.289	1.730	7.1	14
28	2.280	1.731	92.4	17
	2.294			
29	2.214	1.683	59.7	17
	2.221	1.676 ^f		
31	2.410		101.4	17
32	2.342		55.0	17
35			10.9	17
37	2.34	1.745, 1.748	24.1	18
38	2.328	1.82	24.53	19
40, R = CH ₂ NMe ₂	2.408	2.046	124.9	20
45			116.32	21
46			71.2	22
47			54.3	22

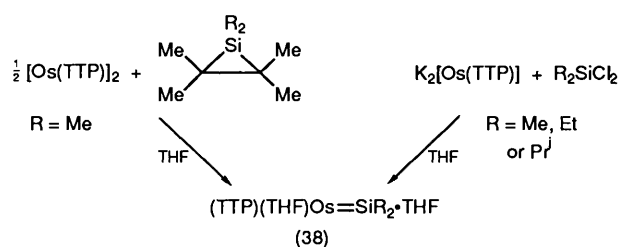
^a Distance to donor atom, N or O. ^b At 23°C. ^c At -60°C. ^d Two isomers present. ^e Three isomers present in solution. ^f Two crystallographically independent molecules present.

which clearly indicates that loss of a silylene ligand does indeed occur.^{15–17}

The base-stabilized silylene complex (26) with sulfur substituents on silicon is reported to form as a mixture together, apparently, with the analogous base-free species (27) in a 1:1.6 ratio.¹⁵ The formation of the base-free complex in a solution containing an equivalent of HMPA is surprising, but it seems that the HMPA is not strongly bound to the Si as the equilibrium can easily be forced to give the adduct by addition of a large excess of HMPA. The reported ^{29}Si NMR chemical shift for the base-free species of 83.2 ppm is also surprising as it is similar to the value of 74.0 ppm for the HMPA adduct [compare 58.3 ppm for the base-stabilized complex (3; R = *p*-tolyl) and 250.6 ppm for its base-free analogue]. A structural study of the base-free compound (27) would clearly be of great interest.

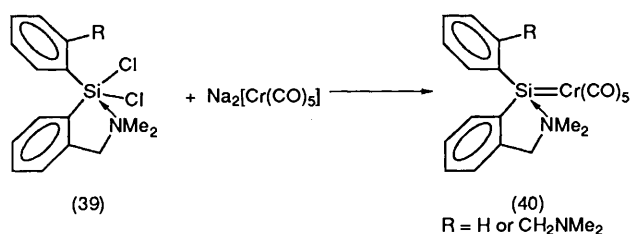
Donor-stabilized osmium silylene complexes (38) in which the osmium is coordinated to *meso*-tetra-*p*-tolylporphyrin (TTP) have been prepared by two routes as shown below. Use of Ph_2SiCl_2 or Bu^tSiCl_2 in the reactions with $\text{K}_2[\text{Os}(\text{TTP})]$ does not afford silylene products, owing presumably to steric factors.¹⁹

The THF is readily displaced from the silicon in (38) by pyridine to give $(\text{TTP})(\text{THF})\text{Os}=\text{SiR}_2$ -pyridine complexes. The chemical shift of the silicon in $(\text{TTP})(\text{THF})\text{Os}=\text{SiEt}_2\cdot\text{THF}$ is 24.53 ppm, in the range now expected for a base-stabilized silylene complex. The crystal structure of $(\text{TTP})(\text{THF})\text{Os}=\text{SiEt}_2\cdot\text{THF}$ shows a short $\text{Os}=\text{Si}$ distance and a long $\text{Si}\cdots\text{O}$ distance in a manner similar to the Fe and Ru complexes



discussed above. The Os–Si–C bond angles of $121(1)$ and $117(10)^\circ$ are also close to those expected for sp^2 hybridized silicon.¹⁹

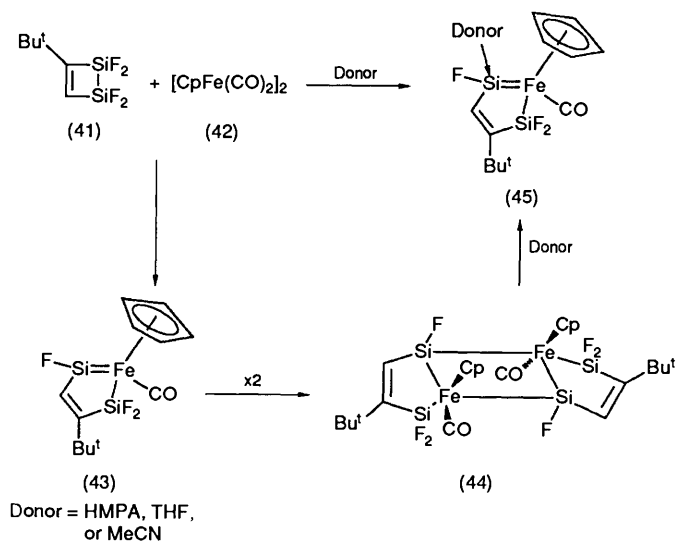
Silylene complexes stabilized by intramolecular base coordination can also be prepared by the salt elimination method. Thus treatment of the five-coordinate silicon compounds (39) give the chromium complexes (40).²⁰



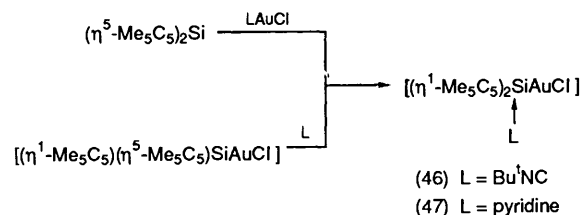
The ^{29}Si NMR chemical shift for (40; $\text{R} = \text{CH}_2\text{NMe}_2$) is temperature dependent (124.9 ppm at 22°C), the shift varying due to the degree to which the amine group is coordinated to the silicon. The crystal structure for the $\text{R} = \text{CH}_2\text{NMe}_2$ complex shows a $\text{Cr}=\text{Si}$ distance of $2.408(1)$ Å and an N to Si distance of $2.046(\text{s})$ Å, somewhat longer than in other base-stabilized complexes. This long and weak interaction between the N and Si may be the reason for the reactivity of the compound as, unlike the iron complex (22) discussed in Section 2.2, it reacts with 2,3-dimethylbutadiene and also with CO, PMe_3 , and pyridine.²⁰

2.4 Other Methods of Preparing Metal Silylene Complexes

The reaction between (41) and (42) gives the Fe_2Si_2 ring compound (44) apparently *via* the silylene complex (43). If the reaction is carried out in the presence of HMPA the donor-stabilized complex (45; donor = HMPA) is formed. Surprisingly if a donor (HMPA, THF, or MeCN) is added to the cyclic dimer (44) the Fe_2Si_2 ring is broken and donor-stabilized silylene complexes (45) (donor = HMPA, THF, or MeCN) are formed.²¹



The reaction between the Si^{II} π -complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Si}$ and $(\text{CO})\text{AuCl}$ affords $[(\eta^1\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{SiAuCl}]$ as a dark red powder. The ^{29}Si NMR chemical shift is $+82.8$ ppm (*cf.* -398 ppm for the starting material) and although this complex has a rather special structure the shift could be considered as characteristic of double bonded silicon. This compound could be considered as base-free but, as the silicon interacts with seven atoms, it could also be considered to have some degree of intramolecular base stabilization through its interaction with the Cp^* ligand. Treatment of the gold silylene complex with Bu^tNC or pyridine leads to formation of the silylene complexes (46) (colourless) and (47) (brown). Unfortunately, no structural details of these interesting compounds are yet available.²²



As can be seen in Table I and from the discussions both above and below, the use of NMR spectroscopy and X-ray crystallography are often crucial in the identification of silicon-containing compounds. Although ^{29}Si NMR spectroscopy is potentially a very powerful technique it is still difficult to predict chemical shifts with any degree of accuracy. Great care needs to be exercised when comparing, for example, metal silyl and metal silylene complexes or in estimating what chemical shifts might be for comparable π -complexes and metallacyclopropanes. For a discussion of chemical shifts in transition metal silyl complexes see references 1b and 1c and references therein.

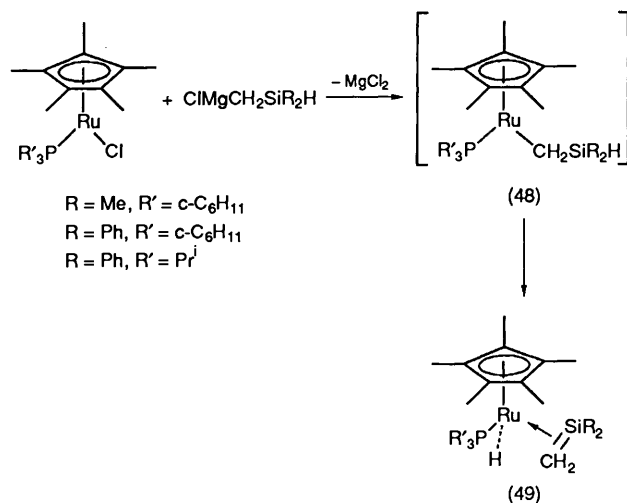
3 Silene, Silatrimethylenemethane, and Silanimine Complexes

No silene complex appears to have been prepared by the simple route of addition of a silene to a transition metal complex. Few attempts at this type of synthesis seem to have been made and this method is likely to be difficult because the bulky substituents which are required for isolation of, for example, the stable silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{C}_{10}\text{H}_{15}$, ($\text{C}_{10}\text{H}_{15}$ = adamantyl), will prevent ready coordination of the double bond to the metal atom. All of the methods so far successful involve formation of the $\text{Si}=\text{C}$ bond within the coordination sphere of the transition metal. References to early work in which transition metal silene complexes were proposed as unstable reaction intermediates are given in references 1b, 1c, and 23.

The bonding in transition metal alkene complexes has been the subject of many investigations and is now usually discussed in terms of the Dewar–Chatt–Duncanson model. This model is based on synergistic σ and π interactions between the alkene p - π and π^* orbitals and suitable metal orbitals which leads to a continuum of structures being possible with extremes of sp^2 (giving an alkene complex) and sp^3 (leading to a metallacyclopropane complex) hybridization at the carbon atoms. The same arguments are possible when considering silene and disilene complexes, and for convenience the structures below are drawn as π -complexes rather than metallacyclopropanes, the real structures actually being somewhere between the two extremes.

3.1 Silene Complexes

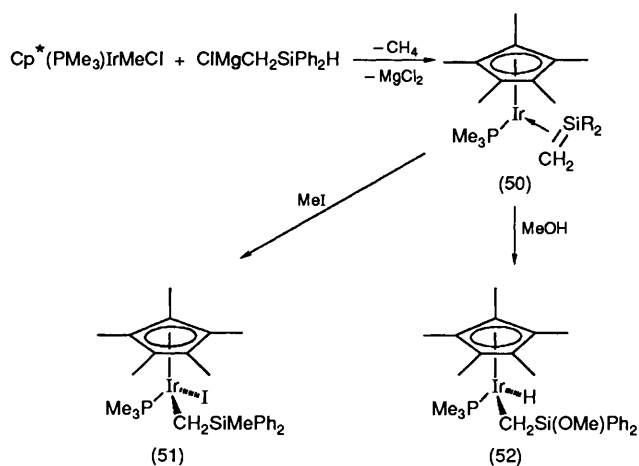
The first isolated η^2 -silene complexes (49) are prepared according to Scheme 2. The compounds seem to be stabilized by the electron-rich ruthenium centre and appear to be formed *via* a β -elimination reaction of the 16 electron species (48) although no evidence for this compound was found by NMR spectroscopy.²³



Scheme 2

The methyl derivative (49; R = Me, R' = Cy), undergoes slow thermal decomposition but complexes (49; R = Ph, R' = Cy; or R = Pr^{*i*}) are thermally stable. The ¹³CH₂ chemical shift for the silene ligand in the two SiPh₂ derivatives is -29.68 and -29.04 ppm respectively and the ²⁹Si chemical shift for the SiMe₂ derivative is 6.14 ppm. The X-ray crystal structure of (49; R = Ph, R' = Pr^{*i*}) shows both enantiomers to be present. The Si=CH₂ bond lengths are 1.78(2) and 1.79(2) Å, indicative of partial double bond character as single Si-C bonds are usually *ca.* 1.87 Å. The Ru-Si-CH₂ bond angles are 63.5 and 64.3° and the hydride is thought to be *cis* to the silicon. Thermal decomposition of the deuteride Cp*(PCy₃)Ru(D)(η²-CH₂SiPh₂) gave Ph₂SiH(CH₂D) as the silicon-containing product which suggests that the decomposition occurs *via* hydride migration to the methylene carbon to give the silyl complex Cp*Ru(PCy₃)Si(CDH₂)Ph₂.²³

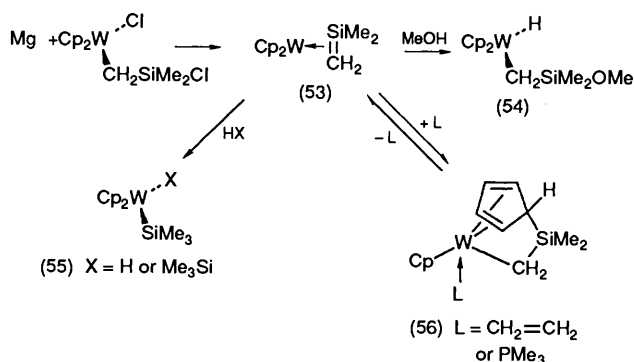
A similar type of reaction gives compound (50) which has a ¹³C chemical shift for the silene carbon of -33.37 ppm. It reacts with MeI and MeOH to give, respectively, complexes (51) and (52), which result from Si-Ir cleavage, but it does not decompose on heating at 140°C in the presence of PMe₃, under UV irradiation in C₆D₆ or when subjected to 100 psi hydrogen.²⁴



A structural study of (50) reveals that the Si-CH₂ distance of 1.810 Å is again shorter than a normal single bond and that the Ir-Si-CH₂ angle is 62.7°. The Ir-Si bond distance of 2.317 Å is relatively short and the Ir-C distance of 2.189 Å relatively long which suggests some π-bonding between the metal and the silene *via* back-bonding. The sum of the C-Si-C angles is 341°, indicative of some *sp*² character at Si, but a little less than in (49) (R = Ph, R' = Pr^{*i*}) in which the sum of the C-Si-C angles is

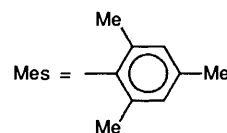
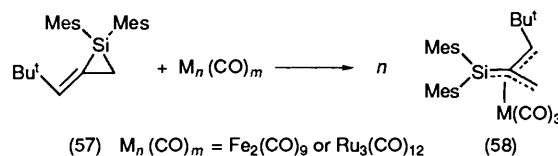
343°. The same preparative route also allows the synthesis of Cp*(PMe₃)Ir(η²-CH₂=SiMe₂) and Cp*(PMe₃)Rh(η²-CH₂=SiPh₂) but these have not yet been isolated in a pure form.²⁴

An alternative synthesis using a dechlorination step allows the preparation of the tungsten silene complex (53). The silene ligand has δ ¹³C for the CH₂ of -41.09 and δ ²⁹Si of -15.7 ppm with coupling constants to W of 28.5 and 57.1 Hz respectively. These coupling constants are smaller than expected for W-C or W-Si σ bonds reflecting low *s*-character and suggest that the bonding is better described as a π-interaction with the Si=C bond.²⁵ Although the W-Si and W-CH₂ bonds (2.534 and 2.329 Å respectively) in (53) are not unusual the Si=CH₂ distance is 1.800 Å which again lies approximately midway between the usual Si-C and Si=C distances of ~1.87 and 1.70-1.76 Å. The sum of the C-Si-C angles around silicon is 348°, also reflecting *sp*² character for the silicon. The compound is also very reactive, giving with methanol the W-C bonded product (54) and with H₂ or Me₃SiH the W-Si bonded products (55). Reactions with ethylene or PMe₃ afford the cyclic products (56).²⁵



3.3 Silatrimethylenemethane Complexes

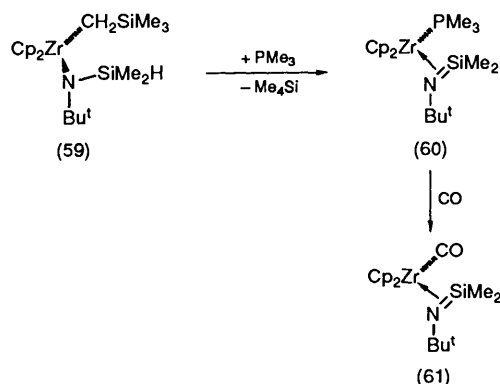
The formation of the air- and moisture-stable η⁴-silatrimethylenemethane complexes (58) occurs on treatment of silirane (57) with a metal carbonyl complex. The ²⁹Si chemical shifts are 43.55 (M = Fe) and 40.12 ppm (M = Ru) which are in the range found for free silenes (*ca.* 40 to 100 ppm). The Si to central carbon bond distance is 1.840 Å in the iron complex, somewhat longer than other silene complexes but shorter than normal Si-C distances. The sum of the angles around the silicon is 346.6°, *i.e.* between *sp*² and *sp*³ hybridization values.²⁶



3.4 Silanimine Complexes

The first transition metal η²-silanimine (R₂Si=NR') ligand-containing complex (60) is formed as the product from the thermal decomposition of the zirconium amide (59) in the presence of PMe₃. The Zr-Si distance is 2.654 Å, somewhat shorter than other reported Zr-Si bonds and the Si-N distance 1.687 Å which is within the range of previously reported Si-N single bonds and longer than those reported for Si=N bonds which suggests that the bonding may better be described as more metallacyclopropane-like. The PMe₃ ligand in (60) is readily

displaced by CO to give (61), which has a ^{29}Si chemical shift of -69.88 ppm, again more indicative of a metallacyclopropane than might be expected for a coordinated silanimine. The sum of the angles around Si in the $\text{Me}_2\text{Si}=\text{NBu}^t$ group is 336.5° .²⁷

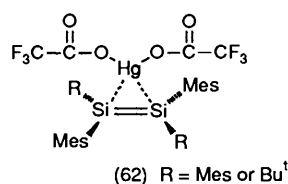


4 Disilene Complexes

Although the chemistry of relatively stable disilenes has, like that of silenes, been investigated for more than a decade, attempts to prepare transition metal complexes have been successful only in the last few years. The obvious synthetic route to try first was that analogous to the method used for the preparation of alkene complexes, *i.e.* addition of a relatively stable disilene to a reactive metal centre. As in silene chemistry, one of the problems associated with this route was that the isolated disilenes available, such as $\text{Mes}_2\text{Si}=\text{SiMes}_2$, all had very large substituents and thus the overlap between the disilene π -bond and metal orbitals could be expected to be poor. Steric repulsions between the bulky substituents on silicon and the other ligands around the transition metal centre would also be expected to lead to poor stability of the complex. Some complexes have, however, been prepared in this way.

4.1 Addition of Stable Disilenes to Transition Metal Complexes

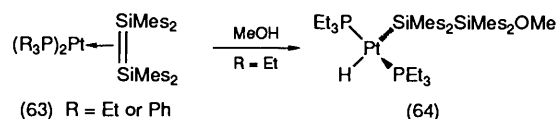
The reaction between $\text{Hg}(\text{OCOCF}_3)_2$ and bulky disilenes $\text{Mes}_2\text{Si}=\text{SiMes}_2$ or the (*E*) or (*Z*) isomers of $\text{Mes}(\text{Bu}^t)\text{Si}=\text{SiMes}(\text{Bu}^t)$ gives 1,2-bis(trifluoroacetoxy)disilanes at room temperature. Below -15°C , NMR spectra of the tetramesityl compound indicate an intermediate in which the mesityl groups are equivalent; it has a ^{29}Si chemical shift of $+8.5$ ppm which suggests a structure of the type (62).²⁸



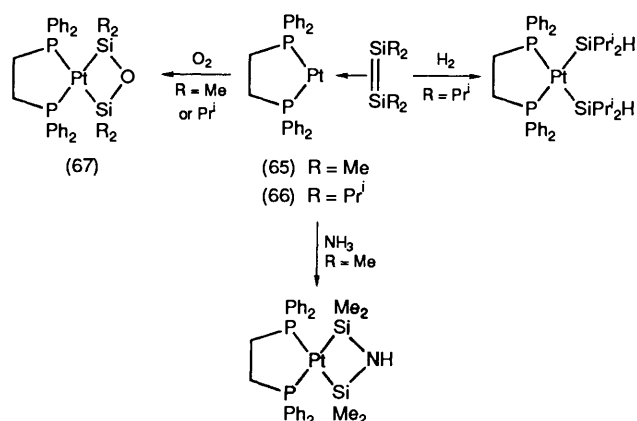
The addition of a bulky disilene to a coordinatively unsaturated platinum fragment, generated from the corresponding platinum oxalate or ethylene complex, also gives disilene complexes (63) in low yield as yellow-orange air-sensitive solids.²⁹ The ^{29}Si NMR chemical shifts for (63; $\text{R} = \text{Et}$ and Ph) are -23.1 and -29.1 ppm respectively and the ^{31}P shifts of 23.3 and 19.5 ppm are similar to those found in ethylene complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{CH}_2=\text{CH}_2)$. The triethylphosphine derivative reacts with methanol with $\text{Pt}-\text{Si}$ cleavage to give (64).²⁹

4.2 Disilene Formation at a Metal Centre

A breakthrough in the preparation of disilene complexes came in changing the synthetic strategy so that the disilene ligand, instead of being preformed and then added to a suitable metal



complex, was actually formed within the coordination sphere of the metal. The successful route involved chemistry derived from the well known ability of transition metals such as platinum to insert into $\text{Si}-\text{H}$ bonds. The first disilene complexes (65) and (66) were thus made using the remarkably simple reactions involving addition of dihydrodisilane, $(\text{R}_2\text{SiH})_2$, to an unsaturated platinum fragment *via* an oxidative addition, reductive elimination reaction sequence.^{29,30} The ^{29}Si chemical shifts for (65) and (66) are 19.60 and -7.84 ppm, *i.e.* between values expected for disilenes and simple three-membered ring compounds. The reaction with H_2 causing $\text{Si}-\text{Si}$ bond cleavage in disilene complexes is of interest since $\text{Pt}-\text{Si}$ bonds are often cleaved by H_2 under mild conditions. Oxidation affords the four-membered ring product (67) in a manner analogous to that of the reaction between $\text{Mes}_2\text{Si}=\text{SiMes}_2$ with O_2 , while ammonia gives a similar product, Scheme 3. These reactions all afford $\text{Si}-\text{Si}$ rather than $\text{Si}-\text{Pt}$ cleaved products.^{29,30}

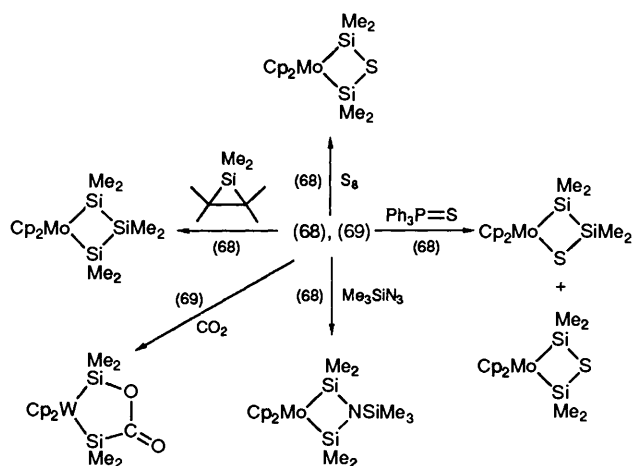


Scheme 3

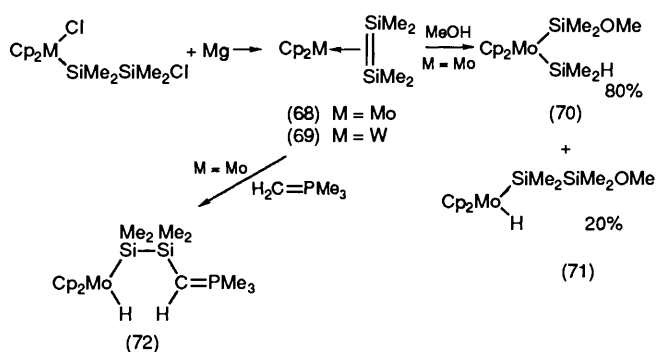
Berry *et al.* have prepared molybdenum and tungsten complexes (68) and (69) of disilenes by a metal reduction route. The ^{29}Si NMR chemical shifts are -20.3 (Mo) and -48.1 (W) ppm ($^1J_{^{183}\text{W}-^{29}\text{Si}} = 50.7$ Hz); the low coupling constant between W and Si compared with other silyl tungsten complexes suggests low *s*-character in that bond and increased *p*-character in the $\text{Si}-\text{Si}$ bond.³⁰ The *X*-ray structure of the tungsten complex shows an $\text{Si}-\text{W}-\text{Si}$ angle of 51.39° , an $\text{Si}-\text{W}$ distance of 2.606 Å, and $\text{Si}-\text{Si}$ distance of 2.260 Å. The $\text{Si}-\text{Si}$ distance is between the expected single and double (2.35 and 2.14 Å respectively) bond lengths. The sum of the angles at each silicon subtended by the methyl groups and the other silicon is 348.3° (between the 360 and 329.1° for ideal sp^2 and sp^3 , respectively). The data all suggest that the Si_2Me_4 ligand in this complex has a nature between that of disilene and that of a disilametallacycle.³¹

The chemistry of $\text{Cp}_2\text{M}(\eta^2-\text{Me}_2\text{Si}=\text{SiMe}_2)$ ($\text{M} = \text{Mo}$ or W) has been investigated. The compounds have similar reactivity and give products that are either the result of reactions reminiscent of metallacyclopropanes or those of coordinated double bonds. Reaction with methanol or $\text{H}_2\text{C}=\text{PMe}_3$ affords compounds (70), (71), and (72) that may be regarded as ring-opened products.³²

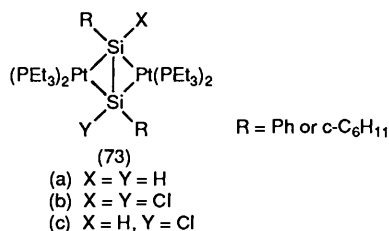
The reactions of (68) with sulfur, $\text{Ph}_3\text{P}=\text{S}$, Me_3SiN_3 , and hexamethylsilylacyclopropane lead to products, Scheme 4, in which ring expansion due to insertion of a single atom has occurred. The reaction of the tungsten complex (69) with carbon dioxide gives a product that is the result of a two-atom insertion into the WSi_2 ring.³²



Scheme 4



The reaction between $(\text{PEt}_3)_2\text{PtCl}_2$ and PhSiH_3 or $(\text{c-C}_6\text{H}_{11})\text{SiH}_3$ in the presence of sodium affords mixtures of complexes (73) in low yield as air-stable yellow crystals. The three phenyl-containing compounds co-crystallize, but the dichloride can be separated by crystallization. The crystal structures of both the co-crystallized mixture and the pure dichloride show the Pt_2Si_2 ring to be puckered and to have a Si-Si distance of 2.575–2.602 Å which is long but within the range of known Si-Si single bond distances.³³ In the cyclohexyl case, a mixture of *cis* and *trans* isomers is formed. *X*-Ray crystallography shows for the *cis* dihydride an angle of 132.3° between the two SiPtSi planes and a Si-Si distance of 2.648 Å, and for the co-crystallized mixture of *trans* (73; a–c) a Si-Si distance of 2.554 Å.³⁴



The bonding in these compounds has been suggested as possibly like π -coordination of a μ_2 - η^2 -disilene ligand to two platinum centres.^{34,35} Molecular orbital calculations on the model complexes $(\text{PH}_3)_4\text{Pt}_2(\text{SiPhCl})_2$ suggest that there is no bonding between the Pt atoms and that the silyl ligand acts as a disilene coordinating to the platinum atom *via* π -donation and back donation to π^* orbitals.³⁵

5 Conclusion

All the transition metal complexes of silylenes, silenes, and disilenes described above as isolated and characterized have

been reported in the past four to five years, and this field of organometallic chemistry can thus be seen as both new and vigorous. Now that several general synthetic routes to these compounds exist it can be expected that many more compounds will be prepared rapidly and their chemistry explored. Larger numbers of each type of complex will be required before structural and spectroscopic trends can be proposed with confidence, and complexes of silicon-containing ligands with a wider variety of transition metals will allow comparisons with analogous carbon compounds. The use of transition metal alkene complexes in catalytic processes suggests that silene complexes may also have industrial importance in, for example, the preparation of polycarbosilanes. Now that silicon analogues to carbyne complexes and silanimine complexes have recently been prepared the scope for new classes of compound is expanding and this field of work looks set for considerable exciting growth in the next few years.

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