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Synthesis and Characterization of Methoxy-bridged Bis(silylene)tungsten Complexes

R. Begum* **and S. M. S. Islam**

Department of Chemistry, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

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Abstract

Synthesis of two methoxy bridged bis(silylene) complexes $(Cp^{Me4})W(CO)_2\{(Et_2Si)\bullet\bullet OMe\bullet\bullet(SiMe_2)\}$(**3**) and $(Cp^{Me})W(CO)_2\{(Et_2Si)\bullet\bullet OMe\bullet\bullet(SiMe_2)\}$(**4**) have been synthesized. Both the compounds contain chiral tungsten center and formed via oxidative addition of an Si-H bond to a coordinatively unsaturated metal center. The complexes were characterized by ^1H, ^{13}C, ^{29}Si NMR, IR and elemental analysis. A plausible mechanism of formation is also suggested.

Keywords: Coordinatively unsaturated; Chiral tungsten; Oxidative addition.

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1. Introduction

Silylene complexes have been proposed as reactive intermediates in a number of organosilicon transformations [1-7], however electrophilic nature of silylene ligands implies difficulties on there straightforward synthesis and consequent study on their properties. Efforts to synthesize silylene complexes resulted donor-stabilized silylene [8-14], donor stabilized bis(silylene) [15-19] and extremely donor stabilized sily(silyline) complexes [20]. A schematic diagram of the orbital interaction in donor stabilized silylene complex shows the role of filled d-orbitals of the transition metal atom in stabilizing the sp^2 hybridized silylene by back donation and the contribution of the donor group (a Lewis base) in satisfying the extreme Lewis acidity of the silylene ligand (Fig. 1).

In 1977, Schimdt and Welz [21] first succeeded in isolating a donor-stabilized silylene complex (Fig. 2 a) by the reaction of $Fe(CO)_5$ and $HSiMe_2NEt_2$. However the instability of this silylene complex above -20°c prevented structural characterization. Ten years later

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[*] *Corresponding author*: ruchy01@yahoo.com, rockshana-che@sust.edu

Tilly *et al.* [22] and Zybill *et al.* [23] reported the first fully characterized donor stabilized silylene complexes, stabilized by electron rich metal center and bulky alkoxy substituents, respectively (Figs. 2b, c). Ogino *et al.* [13] reported synthesis of donor stabilized bis(silylene)iron complexes by photolysis of $Cp(Me)_5Fe(CO)_2SiMe_2SiMe(OMe)_2$ (Fig. 2 d).

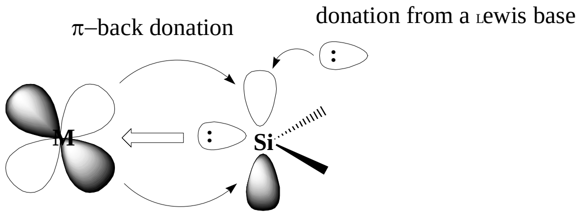


Fig. 1. Schematic diagram of the orbital interaction in donor stabilized silylene complex.

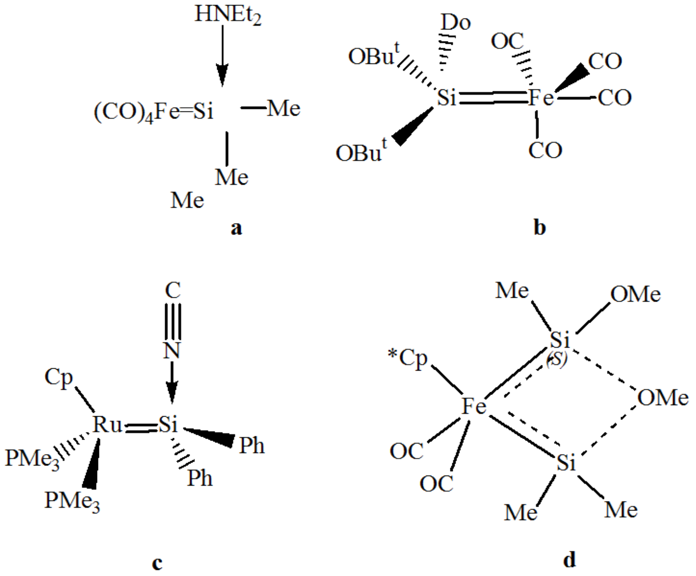


Fig. 2. Donor stabilized silylene complexes.

Because of their involvements in numerous transformation of organosilicon compounds, synthesis and study of complexes featuring silylene ligands are important to understand the mechanism of transformation.

In this paper, synthesis of two methoxy bridged bis(silylene) complexes with chiral tungsten center are reported.

2. Experimental

2.1. *Methods and materials*

All manipulations were performed under a dry N_2 or Ar atmosphere, using standard Schlenk tube techniques, a glove box, or a glove bag. Benzene, pentane, tetrahydrofuran (THF), and diethyl ether (Et_2O) were dried by refluxing over sodium benzophenone ketyl followed by distillation under a dry N_2 atmosphere, immediately prior to use. Diethylamine ($HNEt_2$) and MeOH were dried over CaH_2 and Mg, respectively and distilled under a nitrogen atmosphere before use. $LiAlH_4$ was purchased from 'Wako Pure Chemical' and used as received.

$Cp^{Me}W(CO)_3Me_4$ and $ClSiEt_2SiMe_2Cl$ [24] have been prepared according to the literature. Infrared spectra were obtained by using a HORIBA FT-200 spectrometer. ^1H NMR, ^{13}C NMR, ^{29}Si NMR, spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer. Gas chromatography was carried out with a HITACHI 262-30 gas chromatograph with FID and a SE30/uniport B column (60/80 mesh carrier gas N_2 flow rate: 30 mi/min).

2.2. *Synthesis of $HEt_2SiSiMe_2NEt_2$ [25]*

To a pentane solution (200 ml) of $ClSiEt_2SiMe_2Cl$ (19g, 0.09mol) at 0°C, $HNEt_2$ (16.1g, 0.22 mol) was added with vigorous stirring. After 18 h of continuous stirring at room temperature, the reaction mixture was filtered through a Celite pad. Volatiles were removed from the filtered under reduced pressure. Pale yellow residue was added dropwise with vigorous stirring to a suspension of $LiAlH_4$ (1.26 g) in Et_2O (20 ml) at 0°C. After 30 min of stirring, the reaction mixture was filtered through a Celite pad repeatedly until a clear filtrated was obtained. The filtrate was then distilled under reduced pressure (bp. 107-110°C/20 torr). $HEt_2SiSiMe_2NEt_2$ was obtained as an extremely moisture sensitive liquid (yield 59%) and characterized by ^1H NMR. ^1H NMR (C_6D_6, 300MHz) δ/ppm 3.80 (q, 1H SiH), 2.76 (q, 4H, N$\mathbf{CH_2}$$CH_3$), 1.10 (t, 6H, $SiCH_2$$\mathbf{CH_3}$), 0.95 (t, 6H, $NCH_2$$\mathbf{CH_3}$), 0.7-0.6 (br, 4H, Si$\mathbf{CH_2}$$CH_3$), 025 (s, 6H, Si$\mathbf{CH_3}$).

2.3. *Synthesis of $HEt_2SiSiMe_2OMe$* [25]

To a benzene solution (10 ml) of $HEt_2SiSiMe_2NEt_2$ (10 g, 0.046 mol) MeOH (0.103mol) was added dropwise at 0°C with vigorous stirring. The reaction mixture was stirred at room temperature for 30 min. Distillation of the mixture under atmospheric pressure gave the title compound as a moisture-sensitive liquid (0.029 mol, yield 63%). The compound was characterized by ^1H NMR. ^1H NMR (C_6D_6, 300MHz) δ/ppm 3.77 (q, 1H Si**H**), 3.28

(s, 3H, Si**OMe**), 1.08-1.00 (m, 6H, $SiCH_2\mathbf{CH_3}$), 0.99-0.65 (m, 4H, $Si\mathbf{CH_2}CH_3$), 0.25(s, 6H, $Si\mathbf{CH_3}$).

2.4. *Synthesis of $(Cp^{Me4})W(CO)_3Me$*

To a mixture of $C_5Me_4H_2$ (1.82ml, 0.012mol) and THF (100 ml) BuLi (1.4M solution in *n*-hexane, 8.22ml, 0.012 mol) was added slowly via a syringe at room temperature. After 30 min of stirring $W(CO)_6$ (4.57g, 0.013 mol) was added to the reaction mixture and then refluxed for 50h. CH_3I (0.75g, 0.012 mol) was added dropwise via a syringe with continuous stirring of the reaction mixture. After 4 h stirring at room temperature, volatiles were removed from the reaction mixture using a rotary evaporator. The title compounds were obtained by sublimation of the residue at 0.3 torr/70°C as orange crystal (0.004 mol, yield 33%). The compound was characterized by ^1H NMR, ^{13}C NMR, IR, and elemental analysis. ^1H NMR (C_6D_6, 300MHz) δ/ppm 4.28 (s, 1H C_5Me_4H), 1.53 (s, 6H, $C_5\mathbf{Me_4}H$), 1.40 (m, 6H, $C_5\mathbf{Me_4}H$), 0.38(s, 3H, W-**Me**).

^{13}C NMR (75.5 MHz, tolune-d_8) δ/ppm 232.7 (CO), 105.7 ($\mathbf{C_5}Me_4H$), 102.2 ($\mathbf{C_5}Me_4H$), 87.8 ($\mathbf{C_5}Me_4H$), 11.8 ($C_5\mathbf{Me_4}H$), 11.6 ($C_5\mathbf{Me_4}H$), 25.2 (W-**Me**).

IR (KBr) ν(CO) 1924, 2001 cm^{-1}.

Anal. Calcd. for $C_{13}H_{16}WO_3$: C, 38.64; H, 3.98. Found: C, 38.71; H, 4.01.

2.5. *Synthesis of $(Cp^{Me4})W(CO)_2\{(Et_2Si)\bullet\bullet OMe\bullet\bullet(SiMe_2)\}$(3)*

A Pyrex sample tube (10mm o.d) with a ground glass joint was charged with $(Cp^{Me4})W(CO)_3Me$ (0.12g, 0.27×10^{-3} mol) and $HEt_2SiSiMe_2OMe$ (0.026g, 1.74×10^{-3} mol) and connected to a vacuum line via ground glass joint. About 5ml toluene was transferred to the sample tube by trap-to-trap distillation. The sample tube was then flame sealed under vacuum. The solution was irradiated for 30 min externally with a medium pressure Hg arc lamp (Ushio UV-450) placed in a water cooled quartz jacket. During irradiation, the sample tube was immersed in ice water. The distance from the light source to the sample was ca. 4 cm. After irradiation, the reaction mixture was transferred into a Schlenk tube, concentrated, and cooled to -18°C in a refrigerator to give the title compound as air and moisture sensitive needle-type crystals (0.22 g, yield 81%). The compound was characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, High resolution mass, and elemental analysis. ^1H NMR (C_6D_6, 300MHz) δ/ppm 4.68 (s, 1H $C_5Me_4\mathbf{H}$), 2.82 (s, 6H, Si**OMe**), 1.97 (s, 6H, $C_5\mathbf{Me_4}H$), 1.96 (s, 6H, $C_5\mathbf{Me_4}H$), 1.02 (br, 6H, $SiCH_2\mathbf{CH_3}$), 1.00 (br, 4H, $Si\mathbf{CH_2}CH_3$), 0.58 (br, 6H, $Si\mathbf{CH_3}$).

^{13}C NMR (75.5 MHz, tolune-d_8) δ/ppm 235.9 (**CO**), 107.5 ($\mathbf{C_5}MeH_4$), 105.1 ($\mathbf{C_5}Me_4H$), 93.0 ($\mathbf{C_5}MeH_4$), 57.4 (SiO**Me**), 16.8 ($C_5\mathbf{Me}H_4$), 14.7 ($C_5\mathbf{Me}H_4$), 18.5, 16.4 (Si**Et**), 13.1 (Si**Me**).

^{29}Si NMR (59.6 MHz, tolune-d_8, DEPT) δ/ppm 114.0 ($^1J_{Si\text{-}W}$ = 97.8 Hz), 103.2($^1J_{Si\text{-}W}$ = 100.1Hz).

IR (C_6D_6) ν (CO) 1899, 1830 cm^{-1}.

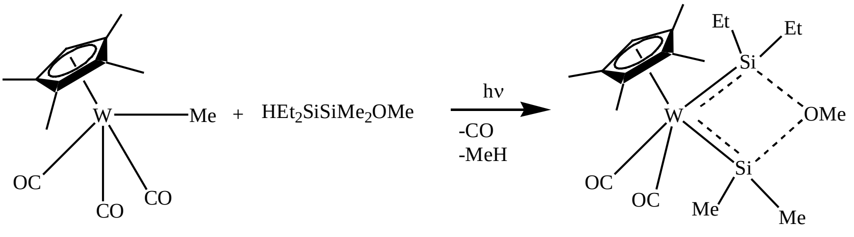
Mass (EI, 70 eV) m/z 536 (M^+, 100), 507 (M^+-Et, 75), 476 (M^+-Et-OMe, 30).
High resolution mass spectrum: Calculated for $C_{18}H_{32}Si_2WO_3$: 536.1400; observed: 536.1407.
Anal. Calcd. for $C_{18}H_{32}Si_2WO_3$: C, 40.24; H, 5.96. Found: C, 40.82; H, 6.16.

2.6. *Synthesis of $(Cp^{Me})W(CO)_2\{(Et_2Si){\bullet\bullet}OMe{\bullet\bullet}(SiMe_2)\}$(4)*

The title compound **4** was synthesized by a similar method described for **3**, using $(Cp^{Me})W(CO)_3Me$ (0.045 g, 0.12×10^{-3} mol) and $HEt_2SiSiMe_2OMe$ (0.066 g, 0.37×10^{-3} mol). Complex **4** was obtained as air and moisture sensitive needle-type yellow crystals (0.036 g, yield 85%). The compound was characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, High resolution mass, and elemental analysis.
^1H NMR (300MHz, tolune-d_8) δ/ppm 4.81 (ddd, 2H, $C_5Me\mathbf{H_4}$), 4.66 (ddd, 2H, $C_5Me\mathbf{H_4}$), 2.81(s, 3H, Si**OMe**), 1.93 (s, 3H, $C_5\mathbf{Me}H_4$), 1.11-0.30 (br, 11H, Si**Et**), 0.31 (br, 6H, Si**Me**).
^{13}C NMR (75.5 MHz, tolune-d_8) δ/ppm 228.5 (**CO**), 105.3 ($\mathbf{C_5}MeH_4$), 88.8 ($\mathbf{C_5}MeH_4$), 52.4 (SiO**Me**), 16.8 ($C_5\mathbf{Me}H_4$), 10.0 ($C_5\mathbf{Me}H_4$), 21.3, 14.5 (Si**Et**), 7.9 (Si**Me**).
^{29}Si NMR (59.6 MHz, tolune-d_8) δ/ppm 114.3 ($^1J_{Si\text{-}W}$ = 96.6 Hz), 102.3 ($^1J_{Si\text{-}W}$ = 98.9 Hz).
IR (C_6D_6) ν (CO) 1907, 1839 cm^{-1}.
Mass (EI, 70 eV) m/z 494 (M^+, 21), 465 (M^+-Et, 12), 323 (M^+-Et-SiOMeSi-CO, 45).
High resolution mass spectrum: Calculated for $C_{15}H_{26}Si_2WO_3$: 494.0896; observed: 494.0919.
Anal. Calcd. for $C_{15}H_{26}Si_2WO_3$: C, 36.43; H, 5.30. Found: C, 36.63; H, 5.61.

3. Results and Discussions

Irradiation of a solution of $(Cp^{Me4})W(CO)_3Me$ and $HEt_2SiSiMe_2OMe$ produces a methoxy-bridged bis(silylene) tungsten complex **3** (Eq. 1).



3

(eq. 1)

^1H NMR spectrum of **3** (Fig. 3) shows a singlet signal for $C_5Me_4\mathbf{H}$ proton at 4.68ppm. Signals for 4 methyl groups of Cp^{Me4} appear as two singlets at 1.97 and 1.96. Appearance of two singlets for two sets of diastereotopic methyls instead of four signals indicated very fast conversion of chirality. Signals of two methyls and two ethyls groups on silicon atom appear as broad signals around 1.1-0.3 ppm because of fast inter-conversion behavior due to silylene-methyl and silylene- ethyl group exchange [24]. For methoxy group, a singlet appears at 2.81 ppm. ^{13}C NMR spectrum of **3** showing only one singlet for two diastereotopic carbonyls also indicates fast conversion of chirality.

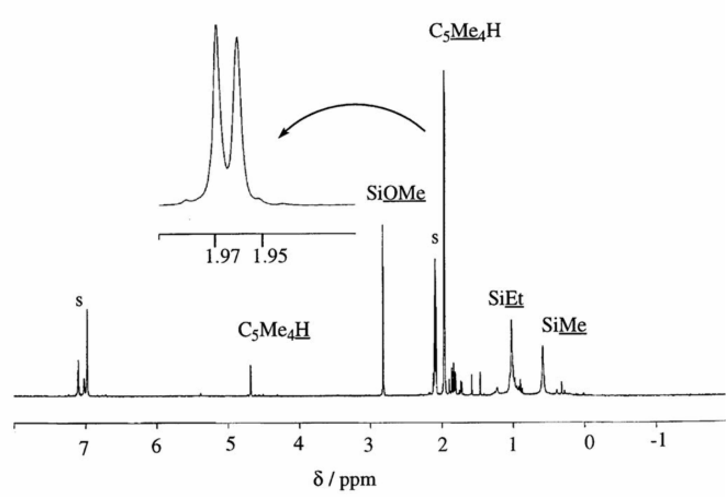


Fig. 3. ^1H NMR spectrum of (300MHz, *tolune-d$_8$*) $(Cp^{Me4})W(CO)_2\{(Et_2Si){\bullet\bullet}OMe{\bullet\bullet}(SiMe_2)\}$(**3**).

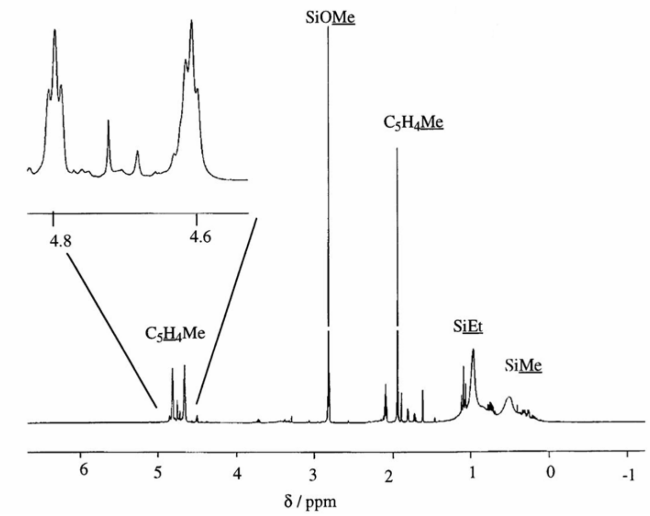
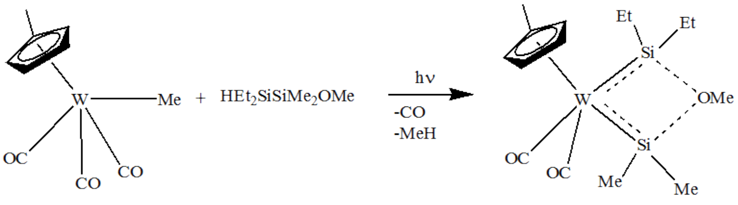


Fig. 4. ^1H NMR spectrum of (300MHz, *tolune-d$_8$*) $(Cp^{Me})W(CO)_2\{(Et_2Si){\bullet\bullet}OMe{\bullet\bullet}(SiMe_2)\}$(**4**).

Irradiation of a solution of $(Cp^{Me})W(CO)_3Me$ and $HEt_2SiSiMe_2OMe$ produces a methoxy- bridged bis(silylene) tungsten complex **4** (Eq. 2).



4

(2)

^{1}H NMR spectrum of **4** (Fig. 4) shows two multiplets for $C_5Me\mathbf{H}_4$ protons at 4.83 and 4.67 ppm. Appearance of two sets of signals for two sets of diastereotopic protons instead of four sets signals indicated very fast conversion of chirality. Signals of two methyls and two ethyls groups on silicon atom appear as broad signals around 1.11-0.3 ppm because of fast inter-conversion behavior due to silylene-methyl and silylene-ethyl group exchange [25]. For methoxy group, a singlet appears at 2.77 ppm. ^{13}C NMR spectrum of **4** shows only one singlet for two diastereotopic carbonyls which also indicates fast conversion of chirality.

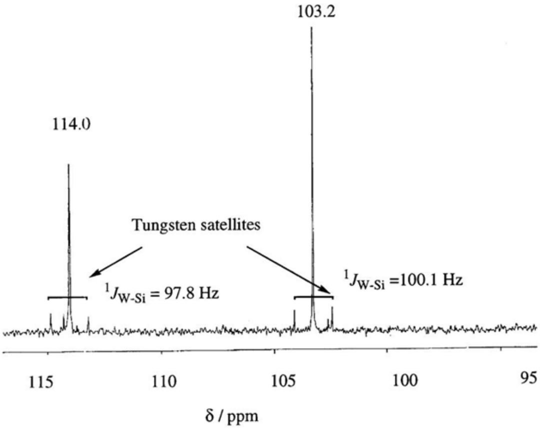


Fig. 5. ^{29}Si NMR (59.6 MHz, tolune-d_8) spectrum of (300MHz, *tolune-*d_8) $(Cp^{Me4})W(CO)_2\{(Et_2Si)$••Ome••$(SiMe_2)\}$ (**4**).

Complex **3** (Fig. 5) shows two ^{29}Si NMR signals at 114.0 ppm. In case of **4** (Fig. 6) two signals appear at 114.3 and 102.3 ppm. Both spectra show tungsten satellites (183W; nuclear spin, I = ½ ; natural abundance, 14.4%) which are very useful indication between bonding of tungsten and silicon in bis(silylene) complex [26]. The coupling constants $^1J_{Si\text{-}W}$ (97.8 and 100.1Hz for **3**, and 96.6 and 98.9 Hz for **4**) directly indicate the contribution of *s* orbital in W-Si bonding. The large values of $^1J_{Si\text{-}W}$ which have been observed for the studied complexes imply unsaturated nature in Si-W bonds [17].

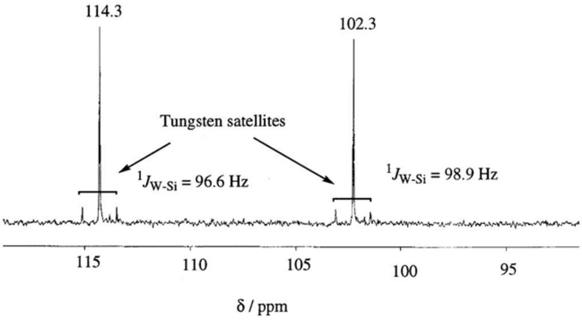
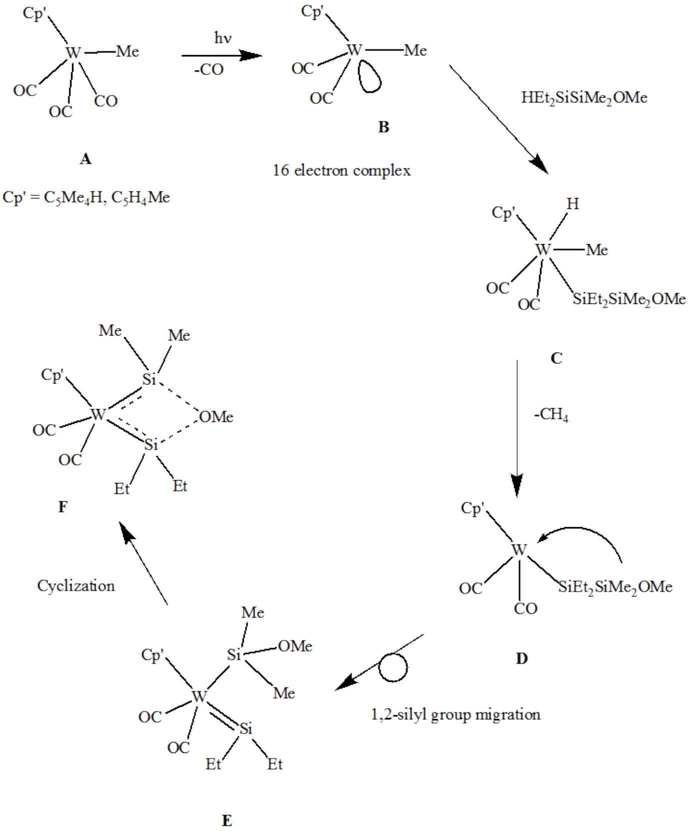


Fig. 6. ^{29}Si NMR (59.6 MHz, tolune-d_8) spectrum of (300MHz, *tolune*-d_8) (Cp^{Me})W(CO)$_2${(Et$_2$Si)•• OMe••(SiMe$_2$)}(**4**).

3.1. *Mechanism of the reaction*

The proposed mechanism for the photolysis of (Cp/)W(CO)$_3$Me in presence HEt$_2$SiSiMe$_2$OMe is shown in Scheme-1.



Scheme-1. Photolysis mechanism of (Cp/)W(CO)$_3$Me.

The proposed mechanism is similar as reported by Wada *et al.* [17] and Ogino *et al.* [13]. The mechanism can be described as i) photochemical elimination of a carbonyl group results in a 16- electron complex **B,** ii) Oxidative addition of a Si-H bond of $HSiEt_2SiMe_2OMe$ to give an 18 electron intermediate **C,** iii) reductive elimination of CH_4 to give a 16 electron complex **D**, iv) 1,2-silyl group migration, and v) cyclization to form a chiral methoxy- bridged bis(silylene) tungsten complex.

4. Conclusion

Synthesis of two methoxy bridged bis(silylene) complexes with chiral tungsten center are reported via oxidative addition of an Si-H bond to a coordinatively unsaturated Tungsten center. The complexes were characterized by IR, ^1H, ^{13}C, ^{29}Si NMR and Elemental analysis. A plausible mechanism of formation is also suggested.

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