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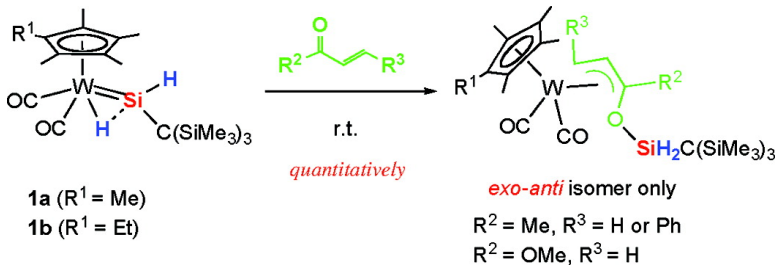

1a (R^1 = Me)
1b (R^1 = Et)

exo-anti isomer only
R^2 = Me, R^3 = H or Ph
R^2 = OMe, R^3 = H

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Reactions of Hydrido(hydrosilylene)tungsten Complexes with α,β-Unsaturated Carbonyl Compounds: Selective Formation of (η^3-Siloxyallyl)tungsten Complexes

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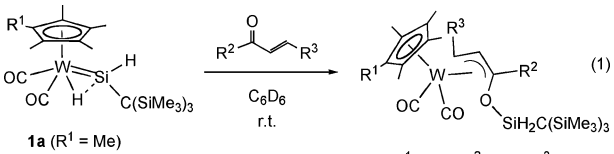
In contrast to that of transition-metal carbene complexes, the development of transition-metal silylene complexes has been slow. Earlier studies on such silylene complexes have concentrated on their syntheses, structures, and fundamental reactions with simple nucleophiles.[1] Recently, because of improved synthetic methodologies, a new stage in the development of silylene complexes has opened.[2−5] For example, a cationic silylene−ruthenium complex has been found to react with enolizable ketones to afford silyl enol ethers.[2] Some silylene complexes, through their M−Si double bonds, can undergo [2+2] cycloaddition reactions with isocyanates.[3] Examples of stoichiometric and catalytic hydrosilylations of alkenes and carbonyl compounds using silylene complexes have also been demonstrated.[4] However, [2+4] cycloaddition reactions involving silylene complexes have yet to be reported.

Recently, we have found the stoichiometric hydrosilylation reactions of acetone[5a] and nitriles[5b] with neutral hydrido(hydrosilylene)tungsten complexes, Cp′(CO)$_2$(H)W═Si(H)[C(SiMe$_3$)$_3$] (**1a**, Cp′ = Cp*; **1b**, Cp′ = η^5-C$_5$Me$_4$Et). Herein, we report on the new and unique reactions of **1** with α,β-unsaturated carbonyl compounds to afford η^3-siloxyallyl complexes. These reactions are highly regioselective, nearly quantitative, and, presumably, proceed via a [2+4] cycloaddition reaction as the main process.

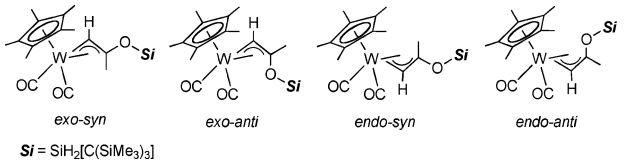
Treatment of hydrido(hydrosilylene)tungsten complex **1a** with methyl vinyl ketone at room temperature resulted in the immediate and quantitative formation of η^3-siloxyallyl complex Cp*(CO)$_2$W-[η^3-H$_2$CCHCMeOSiH$_2${C(SiMe$_3$)$_3$}] (**2a**) as the sole product (eq 1).[6,7] Similarly, the η^5-C$_5$Me$_4$Et analogue, **2b**, was obtained by the reaction of **1b** with methyl vinyl ketone.[6] Transformations of such silylene complexes into the corresponding η^3-allyl complexes have yet to be reported.



(1)

Our synthetic scheme was subsequently applied to other α,β-unsaturated carbonyl compounds. The reaction of **1a** with benzylideneacetone was complete within 10 min to afford Cp*(CO)$_2$W-[η^3-PhHCCHCMeOSiH$_2${C(SiMe$_3$)$_3$}] (**3a**) in 81% isolated yield. The reaction of **1a** with methyl acrylate required more time (24 h) to afford Cp*(CO)$_2$W[η^3-H$_2$CCHC(OMe)OSiH$_2${C(SiMe$_3$)$_3$}] (**4a**) in 82% yield (eq 2). The η^5-C$_5$Me$_4$Et analogues **3b** and **4b** were similarly obtained.[6] In contrast to the linear α,β-unsaturated carbonyl compounds, the reaction of **1a** with cyclohex-2-en-1-one, a cyclic derivative, resulted in a complicated mixture of unidentified products.

Chart 1



All η^3-siloxyallyl products were fully characterized using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis.[6] Existence of the η^3-siloxyallyl ligands was indicated by the ^{1}H NMR spectra. In the case of **2a**, the three ^{1}H signals in the vicinity of 2 ppm were assigned to the central methine proton (δ = 2.08 ppm) and to the terminal methylene protons (δ = 1.47 and 2.40 ppm), and were confirmed using ^{13}C{^{1}H}-^{1}H COSY NMR experiments.[6] The two doublet signals, with AB pattern, at δ = 4.93 and 5.02 ppm ($^2J_{HH}$ = 16.5 Hz) were assigned to the diastereotopic Si−H protons on the siloxy group. The ^{29}Si NMR spectrum of **2a** exhibited signals for the siloxy (δ = −19.9) and the silyl (δ = −0.7) groups. Importantly, in all cases, the formation of a single isomer was observed among four possible isomers, the syn and anti geometrical isomers of the siloxy group in the η^3-allyl ligand and their exo and endo rotomers, as shown in Chart 1.[8]

Structural analysis using X-ray crystallography was employed to determine the stereochemistries of η^3-siloxyallyl complexes **2b**, **3b**, and **4b**.[9] The results indicated that the three complexes have identical stereochemistries[6] (ORTEP drawings of **2b** and **3b** are shown in Figure 1), and possess the exo-anti configuration as illustrated in Chart 1. For all three complexes, the C−C bond between the three allyl carbons [1.405(11)−1.444(10) Å] are shorter than the C−C single bond of ethane (1.54 Å) but longer than the C−C double bond of ethene (1.34 Å), thus supporting their η^3-allyl coordination mode. In all cases, the W−C(5) bond is longer than the W−C(3) and W−C(4) bonds, which can be attributed to the steric repulsion between the carbonyl ligand and the oxygen atom of the siloxy group.

All three η^3-siloxyallyl complexes are suggested to take the exo-anti configuration also in solution, because steric repulsion between the large siloxy and Cp* groups is likely to prevent the formation of other isomers according to the X-ray structures. Similarities between the ^{1}H NMR spectra of the Cp* and the η^5-C$_5$Me$_4$Et analogues (Table S1, in the Supporting Information) further indicate that **2a**, **3a**, and **4a** possess the same exo-anti configuration.[6] Interestingly, the anti selectivity of our methodology is opposite to the syn selectivity for the formation of structurally related Tp-(CO)$_2$Mo[η^3-H$_2$CCHCMeOSi^{t}BuMe$_2$] [Tp = tris-1-(pyrazolyl)-borate],[10] which was obtained using a significantly different route

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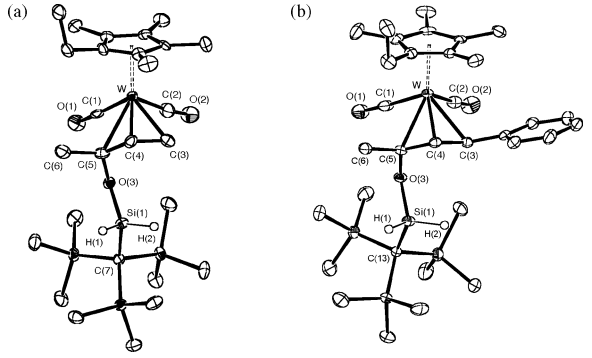
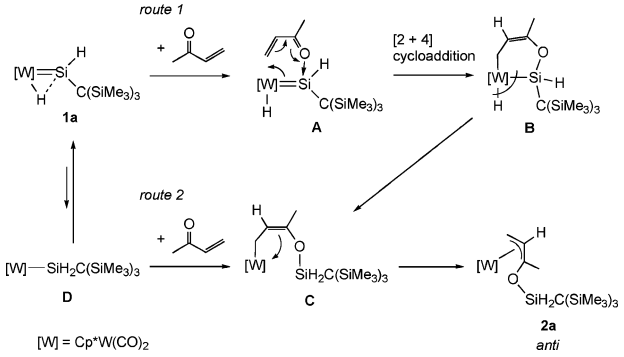


Figure 1. ORTEP drawings of **2b** (a) and **3b** (b) showing 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg). **2b**: W−C(1), 1.966(7); W−C(2), 1.941(7); W−C(3), 2.298(8); W−C(4), 2.223(7); W−C(5), 2.412(6); C(3)−C(4), 1.427(10); C(4)−C(5), 1.444(10); C(5)−O(3), 1.414(8); O(3)−Si(1), 1.650-(6). **3b**: W−C(1), 1.951(5); W−C(2), 1.941(5); W−C(3), 2.343(4); W−C(4), 2.215(4); W−C(5), 2.376(4); C(3)−C(4), 1.418(6); C(4)−C(5), 1.434(6); C(5)−O(3), 1.421(5); O(3)−Si(1), 1.661(3).

Scheme 1. Possible Reaction Mechanisms



involving the reaction between $(DMF)_3Mo(CO)_3$ and methyl vinyl ketone, followed by the addition of ^{t}BuMeSiCl and KTp.

Two most possible reaction mechanisms that explain the high stereoselective formation of the *anti*-η^3-siloxyallyl complex are illustrated in Scheme 1. In route 1, the enone is coordinated to the silicon atom of the silylene ligand of **1a** by the carbonyl oxygen atom to form intermediate **A**, which undergoes a [2+4] cycloaddition via a six-membered transition state to give intermediate **B**. Subsequently, **B** undergoes a Si−H reductive elimination to form 16-electron η^1-allyl intermediate **C**, which is then saturated via coordination of the intramolecular C−C double bond, followed by rearrangement to form *anti*-η^3-siloxyallyl complex **2a**. In route 2, the 16-electron silyl complex **D**, which is formed from **1a** by a 1,2-hydrogen migration from W to Si, reacts with the enone to afford **C**, which then rearranges to **2a**.

Murai et al. have previously reported on the reaction between silyl complex $(CO)_4CoSiMe_3$ and methyl vinyl ketone to give $(CO)_3Co[\eta^3\text{-}H_2CCHCMeOSiMe_3]$ as a mixture of the syn and anti isomers (syn, 12% yield; anti, 46% yield). For reactions with other α,β-unsaturated carbonyl compounds, the syn/anti selectivity greatly depends on the substituents. Because details of the mechanism remain unclear,[11] it is difficult to select route 2 (via silyl intermediate **D**) as the only mechanism to describe the formation of the anti isomer. In our opinion, route 1 is more likely, not only because of the exclusive formation of the anti isomer, but also because of the unsuccessful formation of the η^3-siloxyallyl complex using **1a** and cyclohex-2-en-1-one, which does not allow the *s*-cis conformation required for the [2+4] cycloaddition. Although direct observation of **A** has yet to be achieved, there is evidence that indicates the interaction between the oxygen atom of a ketone with the silylene silicon atom of **1a**. Treatment of **1a** with acetone at 250 K resulted in the formation of $Cp^*(CO)_2(H)_2WSi(H)[OC(Me)=CH_2][C(SiMe_3)_3]$ (**5**),[12] via coordination of the oxygen atom of acetone to the silylene silicon, followed by the α-H migration to W, although **5** is transformed into the hydrosilylation product upon warming to room temperature.[5a] This would support that **A** is a key intermediate of route 1 (Scheme 1).[13]

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Supporting Information Available: Experimental procedures and characterization data; X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) See the Supporting Information for details.

(7) **2a**: ^{1}H NMR (300 MHz, C_6D_6): δ = 0.33 (s, 27H, SiMe), 1.47 (dd, 1H, η^3-H_2CCHCMe, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 6.9 Hz), 1.55 (s, 15H, C_5Me_5), 2.08 (dd, 1H, η^3-H_2CC*H*CMe, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 6.9 Hz), 2.19 (s, 3H, η^3-H_2CCHC*Me*), 2.40 (dd, 1H, η^3-*H*$_2$CCHCMe, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 9.1 Hz), 4.93 (d, 1H, SiH, $^2J_{HH}$ = 16.5 Hz), 5.02 (d, 1H, SiH, $^2J_{HH}$ = 16.5 Hz).

(8) For the definition of exo and anti isomers of η^3-allyl complexes, see: Ariafard, A.; Lin, Z. *Organometallics* **2005**, *24*, 3800.

(9) Crystal data (150 K) for **2b**: $C_{27}H_{52}O_3Si_4W$; fw = 720.90; orthorhombic; space group $Pna2_1$ (No. 33); a = 13.8869(4) Å, b = 8.9296(4) Å, c = 26.3746(8) Å, V = 3270.6(2) Å^3, density (calcd) 1.464 Mg/m^3, Z = 4. Final R indices R = 0.0374, Rw = 0.0851 for all data, 6991 unique reflections. **3b**: $C_{33}H_{56}O_3Si_4W$; fw = 796.99; monoclinic; space group $P2_1/c$ (No. 14); a = 8.2146(4) Å, b = 31.6002(11) Å, c = 14.2624(3) Å, β = 89.5622(18)°, V = 3702.2(2) Å^3, density (calcd) 1.430 Mg/m^3, Z = 4. Final R indices R = 0.0469, Rw = 0.1052 for all data, 8186 unique reflections. For the data of **4b**, see the Supporting Information. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 608679 for **2b**, No. 608680 for **3b**, and No. 608681 for **4b**).

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(12) Complex **5** was not isolable but characterized by ^{1}H, ^{13}C, and ^{29}Si NMR data (250 K).[6]

(13) Besides the mechanisms described in Scheme 1, the possibility of the [2+2] cycloaddition mechanism suggested by a reviewer cannot be ruled out. But we think at present that the mechanisms described in Scheme 1 are more preferable, because the [2+2] cycloaddition mechanism cannot fully explain the absolute anti selectivity of the products.

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