Oxidative Addition of a Si−C(sp) Bond to Ruthenium: Synthesis and Reactivity of $Ru(SiMe_3)(C{\equiv}CSiMe_3)(CO)(P^tBu_2Me)_2$

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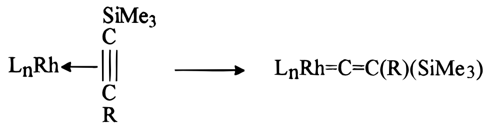
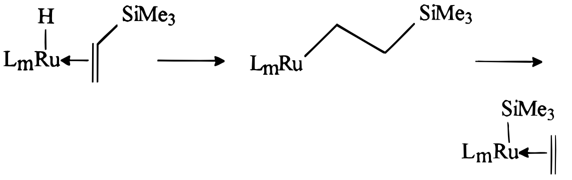
Summary: $Me_3SiC{\equiv}CSiMe_3$ reacts with $Ru(H)_2(CO)L_2$ ($L = P^tBu_2Me$) to give $Ru(SiMe_3)(CCSiMe_3)(CO)L_2$, characterized by solution spectroscopic and single-crystal X-ray diffraction methods. The molecule is square-pyramidal with an apical $SiMe_3$ group and CO and $CCSiMe_3$ in mutually trans basal sites.

Examples of scission of Si−C bonds by transition metals at 25 °C are rare but not unknown. Several examples of an η^2-Me_3SiC_2R complex of Rh have been reported to show 1,2-silyl migration to form vinylidene complexes,[1] either thermally or photochemically (eq 1). However, there are no experimental observations on the mechanism of this migration. Vinylsilanes react with certain metal hydrides to interchange hydride and silyl groups (eq 2), by a mechanism proposed to involve migration of a β-silyl substituent onto the transition metal.[2]



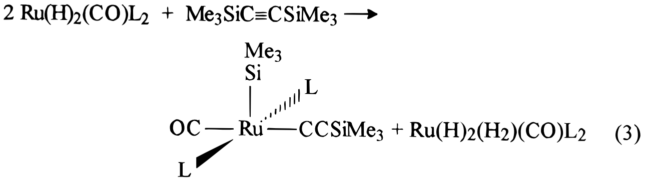
$$L_nRh \leftarrow \begin{matrix} SiMe_3 \\ C \\ ||| \\ C \\ R \end{matrix} \longrightarrow L_nRh{=}C{=}C(R)(SiMe_3) \qquad (1)$$



(2)

We report here several reactions involving unsaturated ruthenium species in which a $Me_3Si{-}C(sp)$ bond is cleaved, with addition of both Si and C to the ruthenium center. Such an addition is unprecedented on reaction with coordinatively unsaturated transition-metal species.

Reaction of $Ru(H)_2(CO)L_2$[3a] ($L = {}^tBu_2MeP$) with excess $Me_3SiC{\equiv}CSiMe_3$ proceeds in toluene or cyclohexane to give 90% $Ru(SiMe_3)(CCSiMe_3)(CO)L_2$ (based on ^{31}P NMR).[4] This molecule was characterized by two $SiMe_3$ ^1H and ^{13}C NMR signals, diastereotopic ^tBu ^1H and ^{13}C NMR signals, and a PMe ^1H NMR virtual triplet (indicating transoid phosphines). Particularly diagnostic are two ^{13}C NMR signals due to sp carbons, one of which (C_α) is a triplet (16.4 Hz) due to coupling to two equivalent phosphorus nuclei. The fate of the two hydride ligands is established to be H_2, which is scavenged by unreacted $Ru(H)_2(CO)L_2$ to give (eq 3) the broad hydride ^1H NMR signals of fluxional $Ru(H)_2(H_2)(CO)L_2$.[3b] $Ru(H)_2(H_2)(CO)L_2$ loses H_2 to re-form $Ru(H)_2(CO)L_2$. The fate of the H_2 is 50% H_2 gas. The other 50% H_2 hydrogenates (see below) excess $Me_3SiC{\equiv}CSiMe_3$ to form *cis*- and *trans*-$(Me_3Si)CH{=}CH(SiMe_3)$, which were identified by characteristic vinyl and trimethylsilyl proton NMR signals. No intermediate is detected when the reaction of eq 3 is monitored by ^{31}P NMR spectroscopy.



(3)

The crystal structure of this product (Figure 1), crystallized from $SiMe_4$, shows the molecule to have a square-pyramidal structure with *trans* phosphines.[5] The silyl group occupies an apical position, showing that this is a stronger σ donor ligand than the acetylide ligand, which is in a basal site and *trans* to CO because this facilitates a push−pull π-donation[6] from the acetylide filled π(CC) orbital. While the trimethylsilyl (cf. tertiary alkyl) group occupies the more crowded apical site, its Ru−Si distance (2.382(2)Å) is only modestly longer than that (2.331(2) Å) in $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$[7] and

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[4] **$Ru(SiMe_3)(CCSiMe_3)(CO)L_2$ ($L = P^tBu_2Me$).** A cold solution of 0.22 mmol of $Ru(H)_2(CO)L_2$ was prepared and diluted with toluene (5 mL). A cold toluene (5 mL) solution of $Me_3SiCCSiMe_3$ (0.05 mL, 0.22 mmol) was added to the red solution. After the mixture was stirred at −75 °C for 3 h, the cold bath was removed and the solution evaporated to dryness. Extraction of the red-orange residue with pentane (2 × 10 mL) and subsequent removal of the volatiles provided a sticky dark red-orange solid. Purification by recrystallization from tetramethylsilane (−40 °C) provides dark red-orange crystals (40%). ^1H NMR (C_6D_6, 23 °C): δ 0.34 (s, 9H, $SiCH_3$), 0.73 (s, 9H, $SiCH_3$), 1.24 (overlapping t, $J_N = 13$ Hz, 36H, PCC*H*3), 1.59 (vt, $N = 5.1$ Hz, 6H, PCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 1.11 (s, Si*C*), 7.93 (t, $J_{PC} = 9.1$ Hz, PCH_3), 13.6 (s, SiC), 30.2 (s, $PCCH_3$), 31.6 (s, $PCCH_3$), 35.33 (vt, $N_{PC} = 16.6$ Hz, $PCCH_3$), 35.7 (vt, $N_{PC} = 16.5$ Hz, $PCCH_3$), 124.8 (s, RuC*C*), 167.2 (t, $J_{PC} = 16.4$ Hz, Ru*C*C), 203.5 (t, $J_{PC} = 11.0$ Hz, Ru*C*O). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 50.1. IR (C_6D_6, cm^{-1}): ν_{CC} 2010, ν_{CO} 1902. Anal. Calcd for $C_{27}H_{60}OP_2RuSi_2$: C, 52.31; H, 9.75. Found: C, 52.70; H, 9.28.

[5] Crystallographic data (−165 °C): $a = 11.168(2)$ Å, $b = 18.043(4)$ Å, $c = 17.746(4)$ Å, $\beta = 108.03(1)°$ with $Z = 4$ in $P2_1/n$. $R(F) = 0.0462$ for 2823 observed ($F > 4\sigma(F)$) data.

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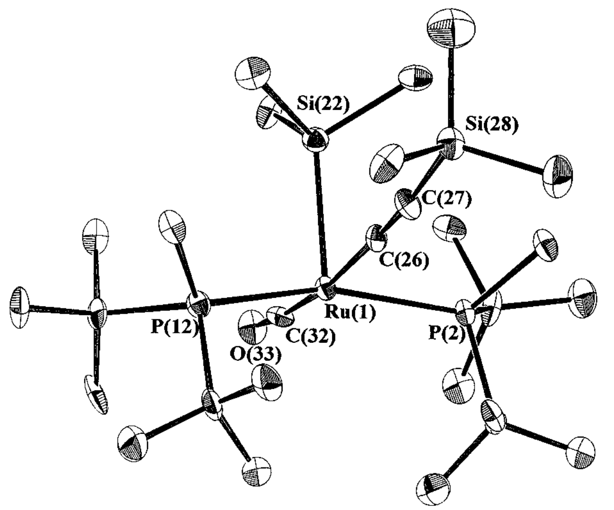


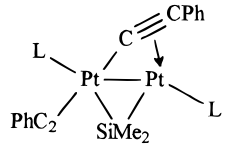
Figure 1. ORTEP drawing of the non-hydrogen atoms of Ru(SiMe$_3$)(CCSiMe$_3$)(CO)(P^{t}Bu$_2$Me)$_2$. Selected bond distances (Å) and angles (deg): Ru−C(26) = 2.048(6), Ru−C(32) = 1.852(7), C(26)−C(27) = 1.216(8); C(26)−Ru−C(32) = 171.3(3), C(32)−Ru−Si = 91.2(2), Ru−C(26)−C(27) = 176.0(6), Ru−C(32)−O(33) = 174.0(6).

it shows no unusual Ru−Si−C angles (range 115.2(3)−116.8(3)°). The most unusual feature of the structure is the acute Si−Ru−C(CSiMe$_3$) angle, 80.2(2)°. Although the Si−C(CSiMe$_3$) distance, 2.87 Å, is certainly nonbonding (the C_3 axis of the SiMe$_3$ group also points directly towards Ru), no comparably acute angle has been observed in square-pyramidal d^6 species.[8] There are no agostic interactions with ruthenium; the closest hydrogen (from a ^{t}Bu methyl) is 2.77 Å from the metal. One ^{t}Bu group from each phosphine projects below the base of the square pyramid, and one methyl of the SiMe$_3$ group eclipses the Ru−C−O bond. Consistent with the presence of the bulky SiMe$_3$ ligand, ∠P−Ru−P is uncharacteristically small (160.73(6)°).

There is supporting evidence that the Si−C bond cleavage is a redox process, requiring zerovalent Ru. Some Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ is formed by Mg reduction of RuCl$_2$(CO)L$_2$ in THF in the presence of Me$_3$SiCCSiMe$_3$.[9] Electron density at Ru is also implicated as an important component of this reaction because Ru(CO)$_2$L$_2$, with one more electron-withdrawing carbonyl ligand than "Ru(CO)L$_2$", fails[10] to react at all (not even adduct formation) with Me$_3$SiCCSiMe$_3$ (although it does oxidatively add the H−C bond of H−CCPh). ^{t}BuC≡CSiMe$_3$ also reacts similarly, giving Ru(SiMe$_3$)(C≡C^{t}Bu)(CO)L$_2$.[11]

The reactivity of Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ observed to date shows ready reductive elimination with re-formation of the Si−C bond. Slow reaction with CO over 12 h produces Ru(CO)$_3$L$_2$ and liberates alkyne, while the complex reacts (70 °C, 12 h) in benzene under argon to liberate alkyne and produce (η^6-C$_6$H$_6$)Ru(CO)L and equimolar L.[10] If excess fluorobenzene is heated (70 °C, 12 h) with Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ in benzene, oxidative addition occurs exclusively to the *ortho* C−H bond of C$_6$H$_5$F. Reaction of Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ with 1 atm of H$_2$ (excess) in benzene at 25 °C gives Ru(H)$_2$(H$_2$)(CO)L$_2$, which hydrogenates the liberated Me$_3$SiCCSiMe$_3$ to *cis*- and *trans-(*Me$_3$Si)HC═CH(SiMe$_3$). Reaction with equimolar Me$_3$SiC≡CH (70 °C, 20 min) gives only partial consumption of Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$, with production of a trace of RuH(CCSiMe$_3$)(CO)L$_2$ along with the major products Ru(*trans*-CH═CH-SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ and Ru(CCSiMe$_3$)$_2$(CO)L$_2$. The last two are known reaction products of the former with Me$_3$SiCCH.[12]

The majority of literature reports on transition-metal/silicon chemistry involve migration of silicon from the metal to carbon.[13] Cleavage of Si−C bonds with coordination of SiR$_3$ has been mainly limited to reports which fail to account for the carbon fragment.[14] However, an especially important exception is the oxidative addition[15] of *both* acetylide substituents of Me$_2$Si(C$_2$Ph)$_2$ to L$_2$Pt(C$_2$H$_4$)$_2$ to give **A**. Two examples are known of



A

Si−C(sp^3) cleavage under mild conditions.[16,17] The reactions reported here should allow for a more detailed determination of whether Si−C(sp) oxidative addition always involves an intermediate η^2-alkyne complex and whether it responds to varying electron donation and withdrawal in RC$_6$H$_4$CC−SiMe$_2$(aryl) substrates, as would be expected for an "oxidative" process.

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Supporting Information Available: Text giving experimental details for the reactions of Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ and tables giving full crystallographic data, positional parameters, and bond lengths and bond angles for Ru(SiMe$_3$)(CCSiMe$_3$)(CO)L$_2$ (7 pages). Ordering information is given on any current masthead page.

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(9) This reaction, which might proceed through "Ru(CO)L$_2$", produces numerous other phosphorus-containing products, perhaps because the reduction in fact proceeds through a Ru(I) species.

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(11) Spectroscopic data of Ru(SiMe$_3$)(CC^{t}Bu)(CO)L$_2$. Anal. Calcd for C$_{28}$H$_{60}$OP$_2$RuSi: C, 55.57; H, 10.01. Found: C, 55.12; H, 9.74. ^{1}H NMR (C$_6$D$_6$, 20 °C): 1.61 (vt, N = 6 Hz, 6H, PCH$_3$), 1.38 (s, 9H, CC(CH$_3$)$_3$), 1.26 (vt, N = 12.6 Hz, 18H, PC(CH$_3$)$_3$), 1.20 (vt, N = 12.6 Hz, 18H, P(CCH$_3$)$_3$), 0.74 (s, Si(CH$_3$)$_3$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 51.65 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): 203.6 (t, J_{PC} = 13 Hz, CO), 126.5 (s, C^tBu), 126.0 (t, J_{PC} = 17 Hz, Ru−CC^{t}Bu), 35.7 (vt, N = 16.2 Hz, P−C(CH$_3$)$_3$), 35.4 (vt, N = 16.2 Hz, PC(CH$_3$)$_3$), 32.2 (s, CC(CH$_3$)$_3$), 31.9 (s, PC(CH$_3$)$_3$), 30.4 (s, PC(CH$_3$)$_3$), 13.9 (s, Si(CH$_3$)$_3$), 7.7 (vt, N = 9.5 Hz, PCH$_3$) ppm. IR (C$_6$D$_6$): ν(CO) 1896, ν(CC) 2150 cm^{-1}.

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