Activation of Water and of Dioxygen by a Bis(diphenylphosphinopropyl)silyl (biPSi) Complex of Ruthenium(II): Formation of Bis(diphenylphosphinopropyl)siloxo Cage Complexes. Concomitant Oxygen Atom Insertion into a Silicon−Carbon Bond

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Summary: The coordinatively saturated hydrido complex $RuH(biPSi)(CO)_2$ (**1**), *biPSi* = $-Si(Me)(CH_2CH_2CH_2PPh_2)_2$, *reacts slowly with either water/piperidine or dioxygen to afford the novel "anchored" siloxo complexes* $RuH[OSiMe(CH_2CH_2CH_2PPh_2)_2](CO)L$ (**3**, L = CO) *and* $RuH[OSi(OMe)(CH_2CH_2CH_2PPh_2)_2](CO)L$ (**6**, L = CO), *respectively, which undergo carbonyl displacement to yield analogues in which* L = $P(OMe)_3$ *that are crystalline* (**5** *or* **7**, *respectively) and for which anti stereochemistry (i.e., H at Ru vs Me or OMe at Si) has been identified by using X-ray crystallography (i.e., products* ***5-a***, ***7-a*** *respectively). Complex* **1** *catalyzes autoxidation of cyclohexene (mainly to cyclohexenone, cyclohexenol: TTO ≈ 300, 4 h).*

Chemical cycles in which either water or oxygen is a primary substrate carry special strategic implications.[1] The industrial requirement for each one as a reagent in olefin functionalization has led to a protracted search for catalyst improvements that may allow the relevant technologies to be optimized. Nevertheless, efficient management of alkene hydration[2] or of related oxidation steps that use elemental oxygen directly[3] is not yet practical under conditions that are fully environmentally acceptable, and indeed the mechanistic fundamentals of either type of chemistry are still imprecisely understood. Oxidative addition of water at a low-valent transition-metal center has repeatedly been suggested as a propagative event in the first of the two contexts, but its immediate products have not often been characterized.[4] The mechanism of homogeneous dioxygen activation, particularly by biomimetic systems, has been deliberated[5] in great detail, but use of the gaseous element directly for selective oxidation of unsaturated organic compounds continues to be regarded[6] as an elusive goal.

We have recently found that both water and dioxygen react slowly along separate and unexpected manifolds with a coordinatively saturated hydrido-complex, $RuH(biPSi)(CO)_2$ (**1**), a ruthenium(II) silyl in which[7] the Ru−Si bond is stabilized by a tridentate framework derived from the silane[8] $SiH(Me)(CH_2CH_2CH_2PPh_2)_2$ (i.e.,[7] biPSiH). The products so obtained share a novel ligand connectivity, in which the Ru-biPSi unit is elaborated into a chelate-supported siloxo cage, nominally by insertion of an oxygen atom into the Ru−Si bond. Most remarkably, the uptake of dioxygen leads to insertion of a second oxygen atom, between silicon and its methyl substituent, thereby generating a methoxysilyl analogue by unprecedented partial oxidation of an inert Si−C bond. We have also observed that in the presence of complex **1** liquid cyclohexene reacts briskly with dioxygen gas (alone, and under ambient conditions), forming autoxidation products in catalytic conversion based on Ru.

Under ^{13}CO gas (1 atm; 25 °C), the hydrido-dicarbonyl[7,9] $RuH(biPSi)(CO)_2$ (diastereomeric mixture:[9] **1-s**,

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1-a) incorporates label only extremely slowly,[9] and accordingly ligand replacement at the d^6 Ru(II) center requires forcing conditions. Thus substitution by $P(OMe)_3$ is effected only after 2 h in refluxing toluene; as expected, it occurs[10] trans to the strongly labilizing silyl group, to afford a single diastereomer that is[11] syn (**2-s**). Although it is unaffected either by water (100 °C; 17 h) or when heated in carefully dried piperidine, compound **1** also reacts with wet piperidine (100 °C; 17 h). The product (**3**) is again detected as a single isomer,[12] the $^{29}Si\{^1H\}$ NMR signal for which is shifted to high frequency vs that of **1** and is observed as a *singlet* (i.e., unlike those[8,9] at δ −2.5, −1.1 for **1-s**, **1-a**, which are triplets, J_{Si-P} 19.7, 11.2 Hz, respectively); it decomposes on attempted isolation, but undergoes facile further reaction with CO (22 °C; 10 min) or $P(OMe)_3$ (78 °C; 20 min), affording analogues **4** and **5**, respectively.[13] Isolation of the phosphite complex **5** as suitable crystals[14] allowed it to be characterized by X-ray crystallography. The molecular geometry, which is shown in Figure 1, immediately explains why the ^{29}Si NMR data[13] for the family **3**−**5** are different from those for **1-s**, **1-a**, and **2-s**: an oxygen atom has entered between Ru and Si of the bound biPSi unit, transforming the latter into a novel tridentate cage that supports a siloxo−ruthenium interaction. The Ru−O and Si−O bond lengths (2.115, 1.605 Å) are both longer and the Ru−O−Si angle (121.7°) is much less obtuse than those[15] in the five-coordinate complex $RuH(OSiPh_3)(CO)(P^tBu_2Me)_2$, while the methyl group on silicon and the hydride occupy opposite faces of the molecule, i.e., the latter is anti,[7] **5-a**.

To elucidate the mechanism of formation of complex **3**, the effect of isotope incorporation was investigated. Allowing precursor **1** to react in ^2H_2O-saturated piperidine, followed by treatment with $P(OMe)_3$, gave rise to sequential formation of the monodeuterio-isotopomers **3-*d*₁** and **5-a-*d*₁** respectively, with the latter showing a broad signal (δ −5.4; $^2J_{P-D}$ 29.5 Hz) in the ^2H NMR and both products showing a very obvious diminution in relative integrated intensity of ^1H NMR signals due to Ru-*H* hydrogens. This observation was checked by examining the effect of H_2O/piperidine on the ^2H-isotopomer[9] **1-*d*₁** of **1**, which led to identification (again by ^1H NMR integration) of hydrido-isotopomers **3** and **5-a** only, with no ^2H NMR signal detectable for the latter and no ^2H incorporation into either during heating (100 °C/3 h) in ^2H_2O-saturated toluene. In a third type of experiment conducted in toluene-d_8 solution in sealed, evacuated NMR tubes, compound **1** was heated with $H_2{}^{17}O$ (20% label) and excess piperidine; after 48 h/105 °C, the ^1H NMR spectrum (high-field range,[12] Ru-*H*) indicated ca. 30% conversion to product, with a new ^{17}O NMR signal (δ 347.0) attributable to label incorporation into **3**, i.e., confirming its formation as a ^{17}O-isotopomer.

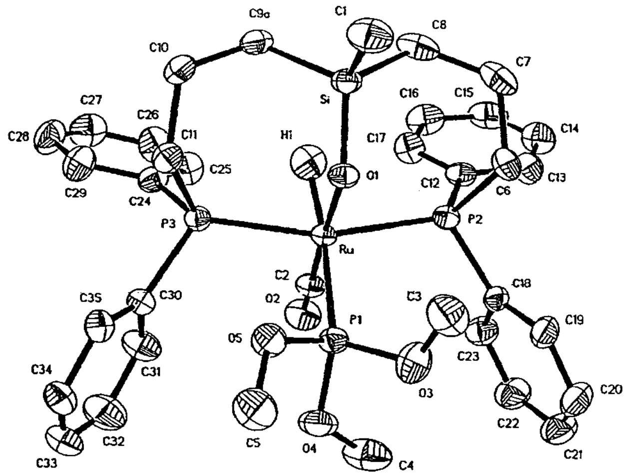

Figure 1. Molecular geometry of complex **5**. Selected bond lengths (Å) and angles (deg): Ru−H(1), 1.62(9); Ru−P(1), 2.366(2); Ru−P(2), 2.353(2); Ru−P(3), 2.348(2); Ru−O(1), 2.115(3); Ru−C(2), 1.823(5); Si−O(1), 1.605(4); Si−C(1), 1.865(7); H(1)−Ru−P(1), 169 (2); H(1)−Ru−P(2), 87 (2); H(1)−Ru−P(3), 77 (2); P(1)−Ru−P(2), 100.6(1); P(1)−Ru−P(3), 95.2(1); P(2)−Ru−P(3), 163.3(1); H(1)−Ru−O(1), 91(2); P(1)−Ru−O(1), 81.0(1); P(2)−Ru−O(1), 88.5(1); P(3)−Ru−O(1), 88.8(1); H(1)−Ru−C(2), 92 (2); P(1)−Ru−C(2), 96.1(1); P(2)−Ru−C(2), 91.1(2); P(3)−Ru−C(2), 92.5(2); O(1)−Ru−C(2), 176.9(2); Ru−O(1)−Si, 121.7(2).

While air appeared to be without effect on solid **1**, very slow (>7 days) oxidation was evident in refluxing benzene solution, affording a new compound **6** essentially quantitatively (>80% yield after recrystallization). The reaction is accelerated by bubbling in oxygen gas, but this leads to formation of coproducts that have not yet been identified. Spectroscopic data[16] for **6** were indicative of a close structural relationship with the prototype **1**, but included unaccountable peaks at δ 3.75 (^1H NMR) and 49.64 (^{13}C); also, as was found for **3**, the $^{29}Si\{^1H\}$ NMR signal is a singlet. Addition of $P(OMe)_3$ yielded (>90%) a diastereomeric derivative **7**, from which the major component[17] was selectively crystallized from diethyl ether, then subsequently shown

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(10) As is established by the magnitude of $^2J_{Si-P}$ (112.4 Hz) in the $^{29}Si\{^1H\}$ NMR spectrum, which with cis coupling (21.3 Hz) to equivalent biPSi nuclei generates a doublet of triplets pattern centered at δ −2.2.

(11) For compound **2**: Anal. Calcd for $C_{35}H_{45}O_4P_3RuSi$: C, 55.91; H, 5.99. Found: C, 55.56; H, 6.06. In NOE difference experiments, on irradiation at the frequency of the ^1H NMR signal attributed to Ru-*H* (δ −6.57, dt), significant intensity enhancement at the frequency of the signal due to Si-C*H*₃ hydrogens (δ 0.46) was evident, and vice versa. Irradiation into Ru-*H* also caused similar enhancement at the $P(OCH_3)_3$ frequency.

(12) Selected spectroscopic data for **3** are as follows: ^1H NMR (C_6D_6, 360.1 MHz): δ 0.36 (SiC*H*₃), −12.65 (t, Ru*H*, $^2J_{PH}$ 21.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 90.6 MHz): δ 203.4 (t, Ru*C*O, $^2J_{PC}$ 14.5 Hz). $^{29}Si\{^1H\}$ NMR (C_7D_8, 49.7 MHz): δ 8.1. $^{31}P\{^1H\}$ NMR (C_6D_6, 145.8 MHz): δ 43.6. The shift of the high-field proton signal is typical for Ru-*H* trans to coordinated heterocyclic N; see for example: Christ, M. L.; Sabo-Etienne, S.; Chung, G.; Chaudret, B. *Inorg. Chem.* **1994**, *33*, 5316.

(13) Selected data for compounds **4** and **5** are as follows. Compound **4**: ^1H NMR: δ 0.46 (SiC*H*₃), −4.17 (t, Ru*H*, $^2J_{PH}$ 23.5 Hz). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 7.9. $^{31}P\{^1H\}$ NMR: δ 33.9. IR: ν(CO) 2048 (s), 1948 (s) cm^{-1}. This product was always contaminated by small amounts of impurity due to decomposition of residual **3** as volatiles were removed from the reaction mixture. Compound **5**: Anal. Calcd for $C_{35}H_{45}O_5P_3RuSi$: C, 54.75; H, 5.87. Found: C, 54.53; H, 5.54. ^1H NMR: δ 0.35 (SiC*H*₃), −5.40 (dt, Ru*H*, $^2J_{PHtrans}$ 185.4, $^2J_{PHcis}$ 21.5 Hz). $^{13}C\{^1H\}$ NMR: δ 203.1 (q, Ru*C*O, both $^2J_{PC}$ 13.2 Hz). $^{29}Si\{^1H\}$ NMR: δ 4.6. $^{31}P\{^1H\}$ NMR: δ 135.7 (t, $^2J_{P-P}$ 24.4 Hz), 40.0 (d). IR: ν(CO) 1904 cm^{-1}.

(14) Crystal data for **5**: $C_{35}H_{45}O_5P_3RuSi$, $M = 767.8$, triclinic, $P\bar{1}$, $a = 9.042(1)$ Å, $b = 12.040(1)$ Å, $c = 18.046(2)$ Å, $\alpha = 95.11(1)°$, $\beta = 101.65(1)°$, $\gamma = 106.57(1)°$, $V = 1821.6(3)$ Å³, $Z = 2$, $\rho_{calcd} = 1.400$ g cm^{-3}, $F(000) = 796$, $\lambda = 0.71073$ Å, $T = 293$ K, $\mu(Mo\ K\alpha) = 0.634$ mm^{-1}, 8362 unique reflections, 5544 observed reflections refined to a final $R = 0.0512$, $R_w = 0.0564$.

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(16) Selected data for compound **6** (major isomer) are as follows: ^1H NMR: δ 3.75 (SiOC*H*₃), −4.22 (t, Ru*H*, $^2J_{PH}$ 20.3 Hz). $^{13}C\{^1H\}$ NMR: δ 199.7 (t, Ru*C*O, $^2J_{PC}$ 11.9 Hz), 193.1 (t, Ru*C*O, $^2J_{PC}$ 7.1 Hz). $^{29}Si\{^1H\}$ NMR: δ −8.2, $^{31}P\{^1H\}$ NMR: δ 33.8. IR: ν(CO) 2046 (s), 1954 (s) cm^{-1}. The minor isomer, which accounted for ca. 15% of the mixture, showed δ Ru*H* at −4.15 (t, $^2J_{PH}$ 20.3 Hz) in the ^1H NMR.

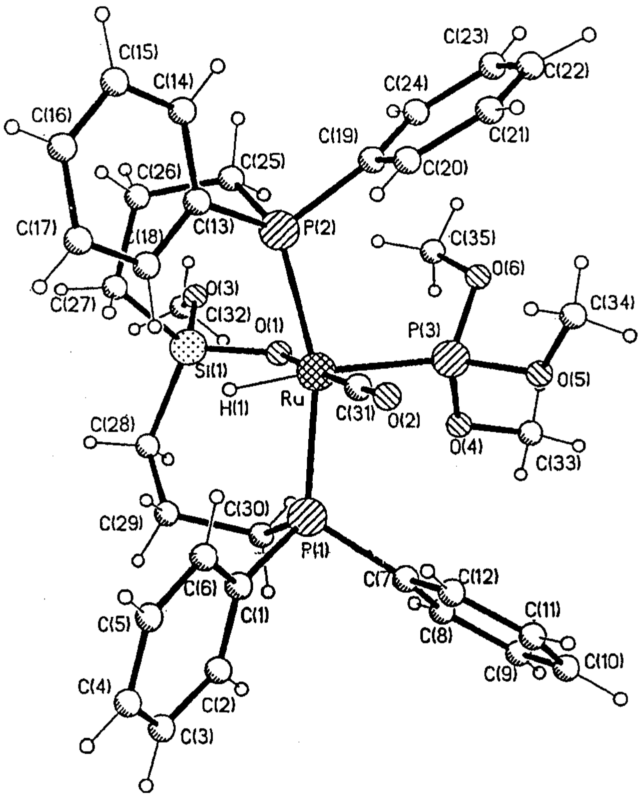

Figure 2. Molecular geometry of complex **7**. Selected bond lengths (Å) and angles (deg): Ru−P(1), 2.351(2); Ru−P(2), 2.352(2); Ru−P(3), 2.364(2); Ru−O(1), 2.111(6); Ru−C(31), 1.82(1); Si−O(1), 1.591(6); Si−O(3), 1.685(9); O(3)−C(32), 1.22(2); P(1)−Ru−P(2), 162.7(1); P(1)−Ru−P(3), 94.4(1); P(2)−Ru−P(3), 102.2(1); P(1)−Ru−O(1), 89.0(2); P(2)−Ru−O(1), 88.6(2); P(3)−Ru−O(1), 80.9(1); P(1)−Ru−C(31), 92.1(3); P(2)−Ru−C(31), 91.4(3); P(3)−Ru−C(31), 95.4(3); O(1)−Ru−C(31), 176.2(3); Ru−O(1)−Si, 127.9(3); O(1)−Si−O(3), 108.3(4); Si−O(3)−C(32), 137 (1).

by using X-ray crystallography[18] to possess the molecular geometry depicted in Figure 2. With Ru−O, O−Si = 2.111, 1.591 Å, respectively, and Ru−O−Si = 127.9°, coordination about Ru closely resembles that in **5-a**. Like that of the latter, the stereochemistry is anti (i.e., **7-a**): a vacancy revealing the position of the hydride ligand is centered on the molecular face opposite of that occupied by the substituent attached to silicon. Unexpectedly, however, the latter contains an oxygen atom, O(3) (with Si−O = 1.69, O−C = 1.22 Å; Si−O−C = 137°): it is a methoxysilyl group, a discovery that explains the otherwise puzzling NMR features observed for[17] **7-a** and[16] **6**. Separate experiments have established that bubbling oxygen gas through solutions of **4** or **5-a** (i.e., rather than **1**, q.v.) converts neither one of these to its Si−O−C-bonded analogue **6** or **7-a**; this might be taken as circumstantial evidence to suggest that both inserted oxygen atoms in **6** originate from the same dioxygen molecule.

The remarkable transformation of coordinatively saturated **1** into its oxygenated derivative **6** led us to screen the system for activity in alkene oxidation. Oxygen gas was bubbled through a frit into mixtures of cyclohexene and 1,2-dichloroethane at ambient temperature. On addition of solid **1** (5×10^{-4} molar equiv vs C_6H_{10}), an immediate color change was evident, to yellow and then deep red. During 4 h, ca. 15% conversion occurred, typically 90% to 2-cyclohexen-1-one and 2-cyclohexen-1-ol with ca. 10% cyclohexene oxide and a trace of *trans*-1,2-cyclohexanediol (TTO[19] ≈ 300). Very similar results were obtained at 5 bar O_2 applied pressure, but significantly at higher catalyst concentration (2×10^{-3} mol equiv) the conversion is actually lower (TTO ≈ 85), and the reaction is shut down by addition of 2,6-di-*tert*-butyl-4-methylphenol. All of these observations are consistent with a catalyzed autoxidation that while reasonably efficient does not appear to be sustainable beyond ca. 20% conversion, at least under the conditions so far applied. Addition of *tert*-butyl hydroperoxide (a familiar co-oxidant[20] in olefin oxidation) to solutions of **1** caused instant formation of black, insoluble material.

The mechanism by which the six-coordinate precursor **1** either undergoes hydrolysis (to **3**) or is oxidized (to **5**) has not yet been ascertained. The requirement for base (i.e., piperidine: with pyridine, a weaker base, parallel chemistry generates an analogue of **3** ca. 4 times more slowly) in its reaction with water is consistent with a transformation to **3** that begins by attack of OH^- (at Si). The fact that the hydrogen isotope bound to Ru in the ultimate product originates exclusively from water (i.e., is *not* carried through from **1**) militates for H_2 (or H^2H) elimination from Ru as a constituent event, but further detail of a sequence into which this fits remains to be determined. The effect of isotope incorporation into compound **6** (i.e., from labeled dioxygen) has not yet been investigated. In view of the saturated state of precursor **1**, however, and in the light of a relevant recent report by Duncan and Hill,[21] initiation of its conversion to **6** by outer sphere electron transfer to give[22] $Ru(III)^+$ and O_2^- (rather than by complexation of molecular dioxygen at the metal center) must be admitted as a serious mechanistic possibility. Ensuing attack by superoxide at Si (or its addition across the Ru−Si bond) would resemble the silyl hydroperoxide-mediated oxidation of alkyl−silicon bonds reported by Tamao et al.[23,24] and could effect the double insertion (into Ru−Si and Si−C) that is required to complete the observed connectivity.

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[17] Selected data for compound **7** are as follows: Anal. Calcd for $C_{35}H_{45}O_6P_3RuSi$: C, 53.63; H, 5.75. Found: C, 53.21; H, 5.62. Major isomer (i.e.,[18] **7-a**): ^{1}H NMR: δ 3.73 (SiOCH_3), −5.44 (dt, RuH, $^2J_{PHtrans}$ 184.7, $^2J_{PHcis}$ 21.3 Hz). ^{13}C{^{1}H} NMR: δ 202.8 (q, RuCO, both $^2J_{PC}$ 13.1 Hz). ^{29}Si{^{1}H} NMR: δ −8.8. ^{31}P{^{1}H} NMR: δ 135.9 (t, $^2J_{P-P}$ 25.0 Hz), 41.6 (d). IR: ν(CO) 1906 cm^{-1}. Minor isomer (ca 15%):[16] δ RuH −5.40 (t, $^2J_{PH}$ 21.5 Hz).

[18] Crystal data for **7**: $C_{35}H_{45}O_6P_3RuSi$, $M = 777.8$, monoclinic, $P2_1/n$, $a = 9.045(2)$ Å, $b = 22.524(2)$ Å, $c = 18.356(2)$ Å, $\beta = 99.63(2)°$, $V = 3687.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.401$ g cm^{-3}, $F(000) = 1612$, $\lambda = 0.71073$ Å, $T = 293$ K, μ(Mo Kα) = 0.629 mm^{-1}, 8475 unique reflections, 3910 observed reflections refined to a final $R = 0.0616$, $R_w = 0.0638$.

[19] Total turnovers, i.e., here corresponding to a minimum TON of 75 h^{-1}.

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