Insight into the Mechanism of the Saegusa Oxidation: Isolation of a Novel Palladium(0)–Tetraolefin Complex

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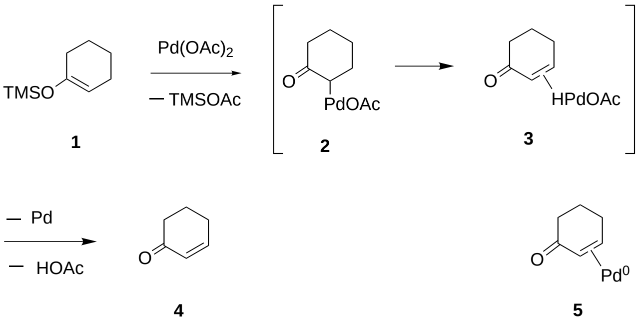
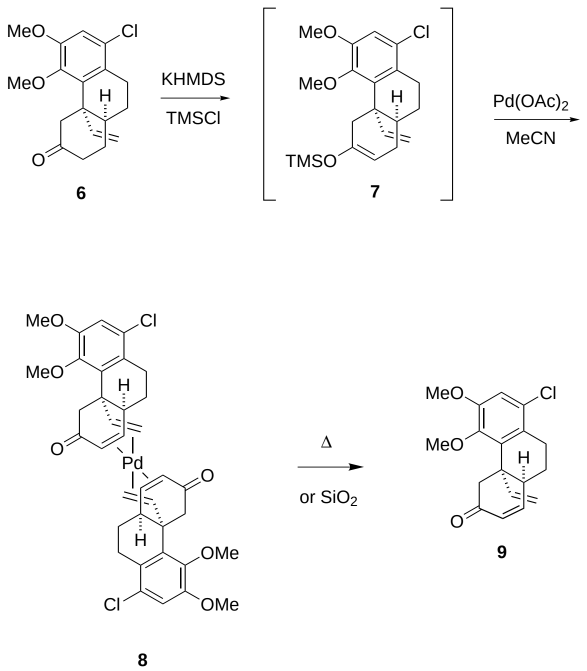
Dedicated to Dr. Gerd Sauer
on the occasion of his 60th birthday

The Saegusa oxidation[1] is a standard method for the conversion of a silyl enol ether (**1**) into the corresponding α,β-enone **4**. The oxidizing agent palladium(II) acetate is added in stoichiometric amounts. In analogy to the Wacker oxidation[2] the formation of a palladium adduct (**2**) is postulated, from which HPdOAc is eliminated to furnish, via complex **3**, the enone **4** (Scheme 1). We now provide evidence that this assumption may not be true in general, and that in suitable cases the palladium is retained in the oxidized substrate as a stable Pd^0–olefin complex (**5**). For the first time, such an intermediate was isolated and characterized as a novel d^{10} Pd^0–tetraolefin complex (**8**).



Scheme 1. Postulated mechanism of the Saegusa oxidation. TMS = trimethylsilyl.

In connection with synthetic studies on hasubanan-type alkaloids,[3] ketone **6** was converted into the silyl enol ether **7** and submitted to the conditions of the Saegusa oxidation (Scheme 2). A brown solid was precipitated from the mixture, which was crystallized and characterized as the palladium complex **8** by NMR and IR spectroscopy (see the Experimental Section), and single-crystal X-ray diffraction[4] (Figure 1). Remarkably, only the C_2-symmetrical diastereomer of **8** was formed. On heating or on treatment with silica gel complex **8** was decomposed to furnish enone **9**, as expected.



Scheme 2. Formation of complex **8** during the Saegusa oxidation of **7**.

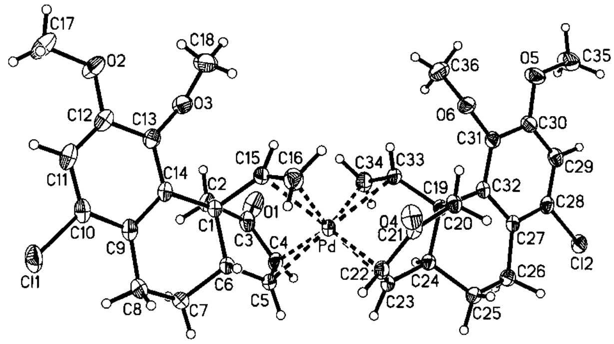


Figure 1. Structure of **8** in the crystal.

A comparison with other d^{10} Pd^0–alkene complexes shows that **8** is highly unusual. Normally such species are unstable and undergo rapid ligand dissociation and oxidation to the corresponding Pd^{II} compounds.[5] Accordingly, stable Pd^0–alkene complexes require electron-deficient alkene ligands with strong d-π backbonding such as dibenzylideneacetone, benzoquinone, or maleic anhydride. The number of coordinated C–C double bonds in these compounds rarely exceeds three, and the coordination geometry is normally trigonal or square planar. Few η^8 Pd^0 complexes have been described (e.g. the unstable [Pd(cod)$_2$][6] or [Pd(benzoquinone)(cod)];[7] cod = cyclooctadiene), and none of these has been characterized by single-crystal X-ray diffraction. Therefore, **8** is the first example of a stable tetrahedral Pd^0–tetraolefin complex whose solid-state geometry has been fully elucidated (Figure 1).

The coordination geometry of **8** is best described as a distorted tetrahedron, the centers of the double bond moieties forming the corners of the tetrahedron. Remarkably, the Pd–C(vinyl) distances are 150–200 pm longer than the Pd–C(enone) distances (Table 1). The length of the enone C–C double bonds are 139.5 and 139.6 pm in **8** and 133.4 pm in the free ligand **9**,[4] which indicates that significant d-π backbonding takes place in **8** from the metal to the enone. Accordingly $\tilde{\nu}$(CO) is 1629 cm^{-1} for **8** and 1675 cm^{-1} for **9**.

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Table 1. Palladium–carbon bond lengths [Å] in **8**.[4]

Pd–C(4): 2.233(2)	Pd–C(22): 2.242(1)
Pd–C(5): 2.153(2)	Pd–C(23): 2.166(1)
Pd–C(15): 2.400(2)	Pd–C(33): 2.345(2)
Pd–C(16): 2.399(2)	Pd–C(34): 2.352(2)

The superposition of the structures (Figure 2) shows that both molecules have similar conformations, especially with respect to the cyclohexenone segment, so that the palladium is trapped by the ligand as soon as it is liberated from the intermediate. In other words, enone **9** is conformationally preorganized to act as a host for the palladium(0) atom. This suggests that the present case is a rather special one, which, however, does provide new information on the mechanism of the Saegusa oxidation, in particular with respect to the decomposition of complexes such as **3**.

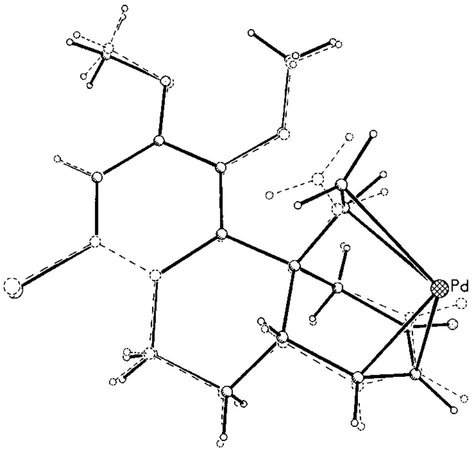

Figure 2. Superposition of the structures of **8** and **9**.

Experimental Section

To a solution of ketone **6** (500 mg, 1.56 mmol) in THF (15 mL) was added KHMDS (4 mL of a 0.5 M solution in toluene, 2.34 mmol) at −78 °C. After the mixture was stirred at −78 °C for 1 h, TMSCl (0.4 mL, 3.12 mmol) was added. The mixture was warmed to room temperature and stirred for an additional hour. Then triethylamine (0.65 mL, 4.68 mmol) was added at 0 °C, followed by diethyl ether (20 mL) and aqueous phosphate buffer (pH 7, 50 mL). The organic layer was washed with brine, dried over sodium sulfate, and concentrated in vacuo. The residue was dissolved in acetonitrile (15 mL), and palladium(II) acetate (420 mg, 1.87 mmol) was added. The mixture was stirred at 50 °C for 2 h and at room temperature for 12 h. The black suspension was filtered, and the precipitate was washed with dichloromethane. On concentration of the filtrate a brown solid was precipitated, which was collected by filtration and recrystallized from chloroform to give pale yellow needles of **8** (464 mg, 80 %). The excess palladium acetate remained in the mother liquor.

8: $C_{36}H_{38}Cl_{2O}O_6Pd$, $M = 744.02\,g\,mol^{-1}$, $R_f = 0.10$ (hexanes:EtOAc 1:1), m.p. 160–163 °C (decomp.); elemental analysis calcd: C 58.12, H 5.15; found: C 58.06, H 5.19; ^1H NMR (400 MHz, $CDCl_3$; the numbering of the H atoms does not correspond to the numbering of the C atoms in Figure 1, but is based on the phenanthrene framework): $\delta = 1.69$ (m, 1H; H-10), 1.94 (m, 1H; H-10), 2.60 (m, 1H; H-9), 2.44 (d, 1H; $J = 17.9$ Hz, H-4), 2.98 (m, 1H; H-9), 2.91 (d, 1H; $J = 17.9$ Hz, H-4), 3.66 (d, 1H, $J = 9.1$ Hz; H-12), 3.79 (s, 6H; OMe), 4.28 (d, 1H, $J = 15.7$ Hz; H-12), 4.45 (br.s, 1H; H-1), 4.79 (d, 1H, $J = 7.4$ Hz; H-2), 5.56 (dd, 1H, $J = 15.5$, 9.8 Hz; H-11), 6.84 (s, 1H; H-7); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 25.69$, 29.25, 38.88, 42.46, 45.29, 55.91, 60.43, 74.69, 82.71, 91.27, 112.72, 118.29, 125.43, 128.62, 138.10, 146.05, 151.30, 195.80; IR (KBr): $\tilde{\nu} = 2936$ (m), 1629 (vs), 1467 (s), 1245 (s), 1216 (m) cm^{-1}; MS (MALDI, sinapinic acid, buffered with ammonium citrate): m/z (%) = 744 (5) [M^+], 424 (15) [Pd+enone], 357 (38) [enone+K^+], 318 (51) [enone], 254 (100), 108 (55) [Pd].

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[2] For the Wacker oxidation, see S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon, Oxford, **1982**, p. 305.

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[4] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-111931 (*rac*-**8**) and CCDC-114053 (*rac*-**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Crystal data: *rac*-**8**: $C_{36}H_{38}Cl_2O_6Pd \cdot 3\,CDCl_3$, triclinic, space group $P\bar{1}$, $a = 11.431(1)$, $b = 14.244(3)$, $c = 14.519(2)$ Å, $\alpha = 76.895(8)$, $\beta = 88.470(8)$, $\gamma = 78.4181)°$, $V = 2255.0(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.623\,g\,cm^{-3}$ at 173 K. A crystal of dimensions $0.28 \times 0.50 \times 0.85$ mm was measured on a SIEMENS SMART diffractometer with $Mo_{K\alpha}$ radiation. An empirical absorption correction using program SADABS gave an effective transmission range from 0.76 to 1.00. Of 35023 reflections measured up to $2\Theta = 61°$, 11388 were independent with $R(I)_{int} = 0.015$; 10991 reflections with $I > 0$ were used. The structure was determined by direct methods using the program SHELXS. The hydrogen atoms were taken from difference Fourier syntheses and were refined with isotropic thermal parameters. $R(F) = 0.031$, $wR(F) = 0.036$, $S = 1.38$ for 679 refined parameters. The final difference density was between -0.10 and $+0.84\,e\,Å^{-3}$. *rac*-**9:** $C_{18}H_{19}ClO_3$, a crystal with approximate dimensions of $0.35 \times 0.25 \times 0.20$ mm was investigated on a NONIUS Kappa CCD diffractometer ($Mo_{K\alpha}$ radiation) at temperatures between 293 and 100 K. The crystal strucure was determined by direct methods (SHELXS-97) and subsequent Fourier and difference Fourier syntheses. The hydrogen atoms were refined with isotropic thermal parameters. Refinements were done with SHELXL-97, 276 parameters were refined. The discussion in the text is based on the data for the measurement at 293 K. 293 K: triclinic, space group $P\bar{1}$, $a = 6.794(10)$, $b = 10.359(2)$, $c = 11.332(2)$ Å, $\alpha = 98.60(3)$, $\beta = 93.86(3)$, $\gamma = 96.89(3)°$, $V = 779.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.357\,g\,cm^{-3}$. Of 5799 reflections measured up to $2\Theta = 53°$, 2921 were independent and 2406 with $F_o > 4\sigma(F_o)$, $R(I)_{int} = 0.015$, were used. $R(F) = 0.040$, $wR(F^2) = 0.114$, $S = 1.052$. The final difference electron density is between 0.16 and $-0.32\,e\,Å^{-3}$. 100 K: triclinic, space group $P\bar{1}$, $a = 6.721(1)$, $b = 10.035(2)$, $c = 11.421(2)$ Å, $\alpha = 98.62(3)$, $\beta = 94.53(3)$, $\gamma = 96.98(1)°$, $V = 752.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.407\,g\,cm^{-3}$. Of 6068 reflections measured up to $2\Theta = 57°$, 3065 were independent and 2747 relections with $F_o > 4\sigma(F_o)$, $R(I)_{int} = 0.015$, were used. $R(F) = 0.032$, $wR(F^2) = 0.090$, $S = 1.096$. The final difference electron density is between 0.33 and $-0.22\,e\,Å^{-3}$.

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