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[31] Abbreviations: CHAPS = 3-[(3-cholamidopropyl)dimethylammonio]propanesulfonic acid, DTT = dithiothreitol, EDTA = ethylenediaminetetraacetic acid, PIPES = piperazine-1,4-bis-(2-ethanesulfonic acid).

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Single-Step Assembly of a C_2-Symmetrical Palladium(IV) Spirocyclic Complex

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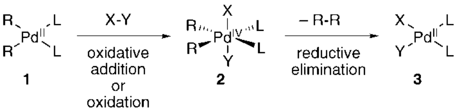
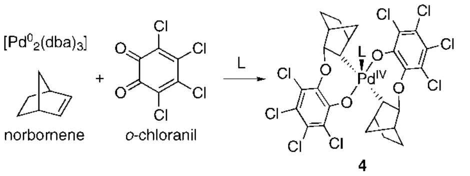
Palladium is an extensively studied transition element in organometallic chemistry as a versatile promoter of various stoichiometric and catalytic organic transformations.[1] Although palladium generally prefers low oxidation states 0, +1, and +2, the involvement of organopalladium(IV) intermediates have been claimed in important catalytic processes.[2,3] In contrast to platinum, which has an extensive organometallic chemistry in the +4 oxidation state,[4] organopalladium(IV) complexes had hardly been studied until the first unequivocal trialkylpalladium(IV) complex, $[PdIMe_3(bpy)]$, was isolated and characterized by X-ray analysis.[5] Since this report, various polyalkylpalladium(IV) complexes **2** were synthesized from dialkylpalladium(II) precursors **1** by oxidative addition of alkylhalides, or oxidation by H_2O, halogens, dichalcogenides, etc., and most of them are thermally labile with the reductive elimination of an alkane readily occuring at or below room temperature to produce the corresponding palladium(II) fragments **3** [Eq. (1)].[6] In striking contrast, we found that the reaction of a readily available palladium(0) complex, $[Pd_2(dba)_3]$ (dba = *trans,trans*-dibenzilideneacetone), with tetrachloro-1,2-benzoquinone (*o*-chloranil) and bicyclo[2.2.1]hept-2-ene (norbornene) directly produced a novel spirocyclic palladium(IV) dialkyl complex **4** in high yield [Eq. (2)].



(1)



(2)

Quinones have received considerable attention in coordination chemistry as redox-active, strongly electron-accepting ligands. Various transition metals have been shown to coordinate to *p*-quinones at their localized ring olefinic bonds.[7] On the other hand, *o*-quinones usually form complexes containing semiquinone or hydroquinone chelate ligands with the concomitant oxidation of transition-metal centers.[8] This was the case for palladium. The reaction of the Pd^0–phosphane complex $[Pd(PPh_3)_4]$ with *o*-chloranil has already been reported to furnish a palladium(II) catecholate complex $[(Ph_3P)_2Pd(O_2C_6Cl_4)]$.[9] Remarkably, the treatment

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of the Pd^0 complex [Pd$_2$(dba)$_3$] with *o*-chloranil (5 equiv) and norbornene (5 equiv) at ambient temperature in acetone followed by addition of diethyl ether produced the palladium(IV) spirocyclic complex **4a** (L = Et$_2$O) in 81 % yield [Eq. (2)]. The absence of the intact *o*-quinone in **4a** was confirmed by its IR spectrum which showed no C=O absorption. The ^{1}H NMR (300 MHz, CDCl$_3$) spectrum showed signals at $\delta = 1.0$–5.0 ppm which were assigned to norbornyl ligands and coordinated diethyl ether. The diethyl ether complex **4a** is readily soluble in acetone, THF, and CHCl$_3$, but it slowly decomposed to deposit black materials in CHCl$_3$. Complex **4a** was quantitatively converted into a thf complex **4b** (L = thf) upon treatment with THF at ambient temperature. To obtain further structural information we characterized **4b** since it is stable in degassed THF at room temperature. The ^{13}C NMR (125 MHz, [D$_8$]THF) spectrum of **4b** showed four signals ($\delta = 117.84$, 122.49, 124.87, and 128.20 ppm) which were assigned to the aromatic C–Cl carbon atoms, and two lower-field signals ($\delta = 144.76$ and 157.24 ppm) were assigned to the aromatic C–O carbon atoms. These observations are indicative of an unsymmetrical tetrachlorocatecholate moiety being present in **4b**. In addition, seven signals observed at higher field ($\delta = 24$–100 ppm) are assigned to norbornane rings in an unsymmetrical environment. The structure of **4b** was unambiguously confirmed by a single-crystal X-ray diffraction study.[10] As shown in Figure 1, **4b** is a dialkylpalladium(IV) complex with a trigonal bipyramidal geometry. Two molecules each of *o*-chloranil and norbornene were coupled on the palladium center to form a pair of unprecedented seven-membered chelete rings. Their O- and C-termini occupy the axial and equatorial positions, respectively. The third equatorial position accommodates a thf molecule. The Pd–O1 and Pd–O3 bonds of 2.0004(13) and 2.0012(13) Å, respectively, are slightly shorter than those in the known Pd^{II} tetrachlorocatecholate complex (2.028(5) and 2.039(5) Å), which are elongated by the *trans* influence of PPh$_3$ ligands.[11] The four C–O bonds in the hydroquinone moieties at 1.320–1.378 Å are close to that expected for a C$_{sp^2}$–O single bond (1.34 Å).[12] The C$_{sp^2}$–C$_{sp^2}$ bonds within the benzene rings (1.390(3)–1.407(2) Å) show no evidence of residual benzoquinone character. The Pd–C bonds of 2.0361(17) and 2.0405(17) Å are similar to those of Pd^{IV}–Me bonds in the precedent examples.[6] All isolated examples of polyalkylpakIladium(IV) complexes to date are confined to octahedral complexes containing bidentate or tripodal donor supporting ligands which prevent the formation of the five-coordinate intermediates that are required for facile reductive elimination of an alkane.[6] On the other hand, the trigonal bipyarmidal complex **4b** is stable in the solid state without any bidentate or tripodal donor spectator ligands. The complete decomposition of **4b** in THF requires several days at ambient temperature. This observation is in contrast to dialkylpalladium(IV) complexes possessing Pd–O$_2$CAr bonds which are unstable at or below 20 °C even though they have tris(pyrazol-1-yl)borate or 2,2′-bipyridyl donor ligands.[13] The remarkable stability of **4** can probably be ascribed to the formation of a chelete ring connecting the labile tetrachlorocatecholate and norbornyl ligands.

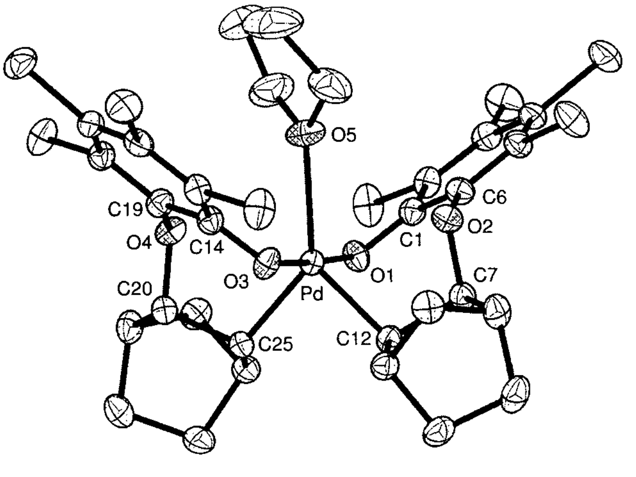

Figure 1. ORTEP diagram of **4b**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-O1 2.0012(13), Pd-O3 2.0004(13), Pd-C12 2.0361(17), Pd-C25 2.0405(17), Pd-O5 2.3751, O1-C1 1.321(2), O3-C14 1.320(2), O2-C6 1.377(2), O4-C19 1.378(2), O2-C7 1.463(2), O4-C20 1.462(2); O1-Pd-O3 177.02(5), C12-Pd-C25 88.98(7), O5-Pd-C12 136.36(6), O5-Pd-C25 134.67(6).

It is noteworthy that the palladaspirocycle framework was possibly assembled through a tandem oxidative cyclization between *o*-chloranil and norbornene on the palladium(0) center. The formation of both the Pd–C and O–C bonds selectively occurred at the less hindered *exo* face of norbornene. The combination of *o*-chloranil and norbornene is quite essential for this process: Employing 3,5-di-*tert*-butylbenzoquinone or 9,10-phenanthrenequinone in place of *o*-chloranil failed to form the corresponding analogues. No product was obtained when less-strained cyclopentene was used as an olefin component. These results show that both the strong oxidizing ability of *o*-chloranil and the ring strain of norbornene play critical roles in the oxidative cyclization.

Figure 2 a shows the ORTEP diagram of **4b** projected down the O5–Pd axis. Interestingly, the palladaspirocyclic framework in **4b** has C_2 symmetry and this is illustrated by a schematic representation in Figure 2 b. The sterically demanding tetrachlorophenyl rings occupy gray quadrants and, as a result, the thf molecule occupies the vacant site in such a way that it is placed along less-hindered colorless quadrants. Such a coordination mode is frequently involved in the enantioface differentiation mechanisms of C_2-chiral asymmetric catalysts.[14] The palladaspirocycle fragment is a potential C_2-symmetrical Lewis acid acceptor bearing the electron-deficient palladium(IV) center. A diethyl ether ligand L in **4** can be replaced by other Lewis basic molecules. In fact, the diethyl ether complex **4a** was dissolved in dry degassed pyridine at ambient temperature to form a new *cis*-bispyridine complex **5**. Figure 3 shows the ORTEP diagram of **5**.[10] To our surprise, **5** has a distorted octahedral geometry with an O1-Pd-O2 angle of 165.32(5)°. Two pyridine molecules are incorporated in the equatorial positions. It is interesting to note that the two tetrachlorophenyl rings are turned away from the coordination sites in the same direction as the norbornane rings. Therefore, the palladaspirocycle framwork has a considerable flexibility to adjust the coordination space to the nature of the coordinated molecules. The coordination number seems to

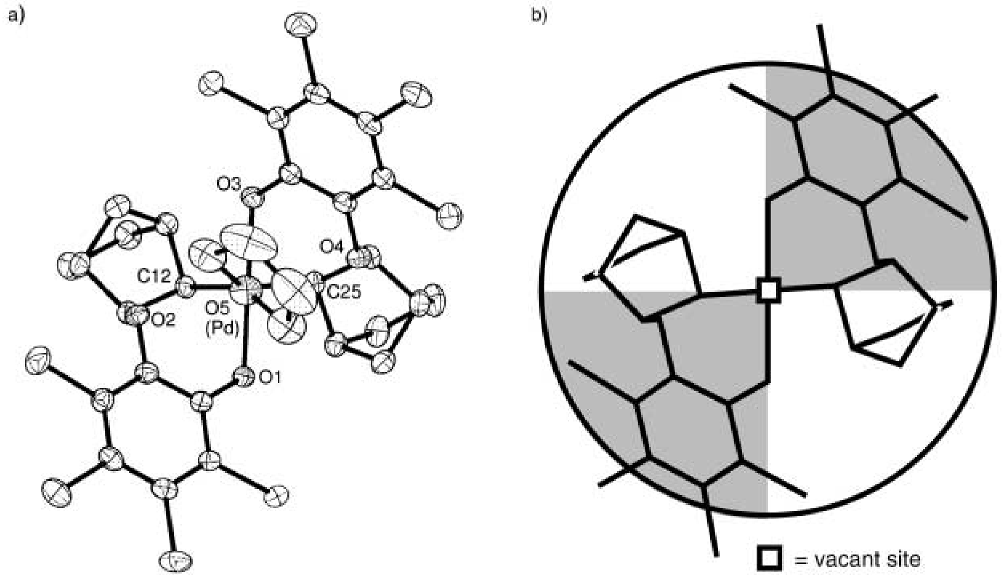

Figure 2. a) ORTEP diagram of **4b** projected down the O5–Pd axis and b) schematic representation of palladaspirocyclic framework.

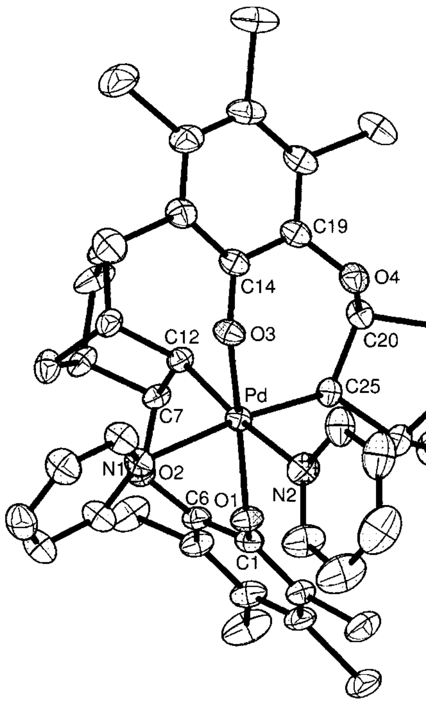

Figure 3. ORTEP diagram of **5**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-O1 2.0248(11), Pd-O3 2.0301(11), Pd-C12 2.0753(15), Pd-C25 2.0741(15), Pd-N1 2.2480(14), Pd-N2 2.2391(15), O1-C1 1.3133(19), O3-C14 1.312(2), O2-C6 1.3630(18), O4-C19 1.356(2), O2-C7 1.4475(18), O4-C20 1.453(2); O1-Pd-O3 165.32(5), C12-Pd-C25 84.51(6), N1-Pd-N2 85.46(5), N1-Pd-C12 95.54(6), N2-Pd-C25 95.59(6).

vary depending on the electron-donating ability of the Lewis base molecules; that is, it increased from five for the weaker thf donor to six for the stronger pyridine donor. In accordance with this observation, the Pd–C12 and Pd–C25 bonds in **5** are longer than those in **4b** by 0.0392 and 0.0336 Å, respectively, as a result of the *trans* influences of the stronger electron-donor pyridine.

In conclusion, we have identified an unprecedented single-step assembly of dialkylpalladium(IV) complex having a novel palladaspirocycle framework from commercially available [$Pd_2(dba)_3$], *o*-chloranil, and norbornene. The palladaspirocycle fragment has C_2 symmetry and functions as a Lewis acid acceptor. The ligand exchange from thf to pyridine caused a geometrical transformation to afford a bispyridine complex with a distorted octahedral geometry. The elucidation of the mechanism for the palladaspirocycle formation and its application to Lewis acid catalysis are now under way.

Experimental Section

4a: A solution of [$Pd_2(dba)_3$]·$CHCl_3$ (155.3 mg, 0.150 mmol), *o*-chloranil (245.9 mg, 0.750 mmol), and norbornene (94.2 mg, 0.750 mmol) in dry degassed acetone (10 mL) was stirred at room temperature for 30 min. The initial purple suspension turned into a red homogeneous solution within 10 min. The resultant solution was filtered through a glass frit and the filtrate was concentrated to 3 mL, diluted with dry degassed diethyl ether (50 mL), and cooled overnight at about −15 °C. The orange crystals obtained were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 209.9 mg (81 %): m.p. 117.3–118.3 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$–1.15 (m, 1 H), 1.21 (t, $J = 7.0$ Hz, 3 H), 1.35–1.46 (m, 1 H), 1.48–1.75 (m, 3 H), 2.66 (d, $J = 4.5$ Hz, 1 H), 2.84 (d, $J = 4.5$ Hz, 1 H), 3.01 (d, $J = 11.5$ Hz, 1 H), 3.48 (q, $J = 7.0$ Hz, 3 H), 4.08 (d, $J = 4.5$ Hz, 1 H), 4.84 ppm (dd, $J = 4.5$, 2.0 Hz, 1 H); elemental analysis calcd (%) for $C_{30}H_{30}Cl_8O_5Pd$ (860.60): C 41.87, H 3.51; found: C 41.60, H 3.53.

4b: The diethyl ether complex **4a** (86.1 mg, 0.10 mmol) was dissolved in dry degassed THF (5 mL) and stirred at room temperature for 30 min. The solution was filtered through a glass frit and the filtrate was concentrated to 1 mL, diluted with dry degassed pentane (10 mL), and cooled overnight at about −15 °C. The orange crystals obtained were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 82.4 mg (96 %): m.p. 109.8–110.0 °C (decomp); ^{1}H NMR (500 MHz, [D_8]THF) $\delta = 1.20$–1.27 (m, 1 H), 1.43–1.49 (m, 1 H), 1.54 (tt, $J = 12.5$, 5.0 Hz, 1 H), 1.65 (d, $J = 11.0$ Hz, 1 H), 1.76–2.66 (m, 4 H), 2.66 (d, $J = 4.5$ Hz, 1 H), 2.75 (d, $J = 5.0$ Hz, 1 H), 2.94 (d, $J = 11.0$ Hz, 1 H), 3.60–3.64 (m, 4 H), 4.10 (d, $J = 4.5$ Hz, 1 H), 4.42 ppm (dd, $J = 5.5$, 2.5 Hz, 1 H); ^{13}C NMR (125 MHz, [D_8]THF) $\delta = 24.73$ (CH_2), 26.39 (CH_2), 27.98 (CH_2), 36.67 (CH_2), 44.44 (CH), 45.83 (CH), 68.22 (CH_2), 78.12 (CH), 98.92 (CH), 117.85, 122.49, 124.87, 128.20, 144.76, 157.24 ppm; FAB-MS *m*/*z* (%) 541

(44) [$M^+ - \text{thf} - C_6Cl_4O_2$], 446 (100) [$MH^+ - \text{thf} - C_6Cl_4O_2 - C_7H_{12}$]; elemental analysis calcd for $C_{30}H_{28}Cl_8O_5Pd$ (858.58): C 41.97, H 3.29; found: C 42.27, H 3.43.

5: The diethyl ether complex **4a** (86.1 mg, 0.10 mmol) was dissolved in dry degassed pyridine (1 mL) and stirred at room temperature for 30 min. The solution was filtered through a glass frit and the filtrate was diluted with dry degassed pentane (30 mL) before being cooled overnight at about −15 °C. The obtained brown crystals were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 76.7 mg (75.6 %): m.p. 99.2–99.5 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$–1.32 (m, 1 H), 1.34–1.46 (m, 1 H), 1.54–1.80 (m, 3 H), 2.71 (d, $J = 3.8$ Hz, 1 H), 2.75 (d, $J = 3.8$ Hz, 1 H), 3.00 (d, $J = 10.2$ Hz, 1 H), 4.03 (s, 2 H), 7.25 (dd, $J = 7.8$, 4.2 Hz, 4 H), 7.67 (tt, $J = 7.8$, 1.5 Hz, 1 H), 8.51 ppm (d, $J = 4.2$ Hz, 4 H); MS (FAB) m/z (%) 541 (34) [$M^+ - 3\,\text{Py} - C_6Cl_4O_2$], 446 (100) [$MH^+ - 3\,\text{Py} - C_6Cl_4O_2 - C_7H_{12}$]; elemental analysis calcd (%) for $C_{41}H_{35}Cl_8N_3O_5Pd$ (1023.78): C 48.10, H 3.45, N 4.10; found: C 47.93, H 3.41, N 3.91.

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[10] Crystallographic data: Intensity data were collected at 173 K on a Bruker SMART APEX diffractometer with $Mo_{K\alpha}$ radiation (0.71073 Å) and graphite monochrometer. The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 (SHELXTL). **4b**: $C_{30}H_{28}Cl_8O_5Pd$, $M_r = 858.58$, space group $P2(1)/n$ (no. 14), monoclinic, $a = 10.0282(7)$, $b = 21.2453(15)$, $c = 15.1970(11)$ Å, $\beta = 90.171(2)°$, $V = 3237.7(4)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.761\ \text{g cm}^{-3}$; a total of 24 938 reflections were measured and 8652 were independent [$R(\text{int}) = 0.0245$]. Final $R_1 = 0.0275$, $wR_2 = 0.0725$ [$I > 2\sigma(I)$], and GOF = 0.743 (for all data, $R_1 = 0.0329$, $wR_2 = 0.0778$). **5**: $C_{41}H_{35}Cl_8N_3O_4Pd$, $M_r = 1023.78$; space group $P\bar{1}$ (no. 2), triclinic, $a = 10.4110(5)$, $b = 12.2527(6)$, $c = 18.4200(9)$ Å, $\alpha = 75.0470(10)$, $\beta = 75.0760(10)$, $\gamma = 66.4740(10)°$, $V = 2049.57(17)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.659\ \text{g cm}^{-3}$; a total of 16 045 reflections were measured and 10 743 were independent [$R(\text{int}) = 0.0203$]. Final $R_1 = 0.0302$, $wR_2 = 0.0811$ [$I > 2\sigma(I)$], and GOF = 0.733 (for all data, $R_1 = 0.0320$, $wR_2 = 0.0832$). CCDC-186953 (**4b**) and CCDC-186954 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Direct Assembly of Large Arrays of Oriented Conducting Polymer Nanowires[**]

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Recently, oriented carbon nanotubes, and nanowires of semiconductors, oxides, and metals have attracted wide attention. However, there have been few reports on the direct growth of oriented polymer nanostructures such as oriented polymer nanowires. Oriented conducting polymer nanostructures will be very useful for many applications,[1–3] which range from chemical and biological sensing and diagnosis to energy conversion and storage (photovoltaic cells, batteries and capacitors, and hydrogen-storage devices), light-emitting display devices, catalysis, drug delivery, separation, microelectronics, and optical storage.

Several methods, which include electrospinning[4,5] and polymer-templated electrochemical synthesis,[6] have been used for preparing conducting polymer nanofibers. Highly porous, conducting polymer films based on techniques such as dip coating on porous supports have been widely investigated for separation and sensing,[7] but the random pore structures and misalignment of the polymers are not ideal for high efficiency and faster kinetics. Controlled orientation is more critical for applications such as in light-emitting and micro-

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