Synthesis and Characterization of a Novel Dialdehyde and Cyclic Anhydride

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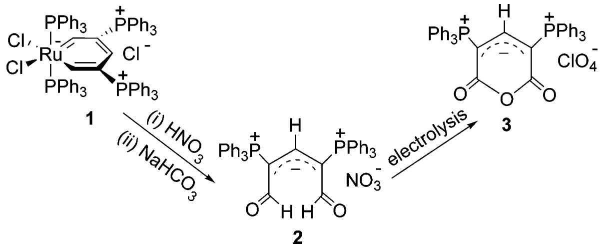
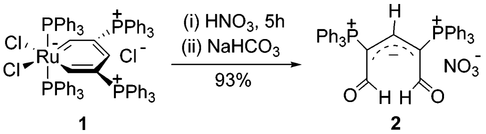


The acid treatment of a ruthenabenzene yielded an unusual dialdehyde. Interestingly, this dialdehyde has notable anti-oxidative properties and resists even nitric acid. This stability is confirmed by chemical and electrochemical experiments. In addition, a stable cyclic anhydride is synthesized from the dialdehyde via an environmentally friendly electrochemical method.

Aldehydes are important and versatile compounds, widely used in organic synthesis.[1,2] Usually, aldehydes are reactive toward oxygen of the air and sunlight and can be slowly oxidized or undergo autopolymerization.

We recently reported the preparation of ruthenabenzene [Ru(CHC(PPh$_3$)CHC(PPh$_3$)CH)(PPh$_3$)$_2$Cl$_2$]Cl (**1**).[3] During the investigation of the stability of the ruthenabenzene, we obtained a novel dialdehyde **2** from the reaction of ruthenabenzene **1** with nitric acid. Because of its surprising air-stability, thermal-stability, and anti-oxidative ability, we have further investigated its electrochemical properties. The investigation led us to isolate a stable cyclic anhydride **3** from the dialdehyde via an electrochemical method.

SCHEME 1. Preparation of Dialdehyde 2



Ruthenabenzene **1** reacted with nitric acid in dichloromethane for 5 h, and then aqueous NaHCO$_3$ was added to neutralize the reaction solution, which led to the formation of compound **2** in 93% yield (Scheme 1). Although compound **2** contains two aldehyde groups and two phosphonium groups, a Wittig dimerizaion or trimerization was not observed during this reaction process.

The structure of **2** has been confirmed by X-ray diffraction. As shown in Figure 1, the C(1)−O(1) (1.211(3) Å) and C(5)−O(2) (1.208(3) Å) bond distances are consistent with the C−O distance of aldehyde groups.[4] For the five sp^2-hybridized carbon atoms, the C−C bond lengths are in the range 1.379(3)−1.429(4) Å and there is no significant C−C bond length alternation, as expected for a delocalized structure. The C$_5$ backbone of **2** is distorted, and the dihedral angle between the C1/C2/C3 plane and the C3/C4/C5 plane is 45.7°, mainly because of the steric hindrance between the two aldehydic hydrogens, which is similar to the twist of the biphenyl moiety in compounds with biphenyl units.[5] In addition, it can be seen that compound **2** contains an allyl anion structure consisting of the three sp^2-hybridized carbon atoms C2, C3, and C4, which is usually encountered as a ligand in organometallic compounds but seldom observed in organic compounds.

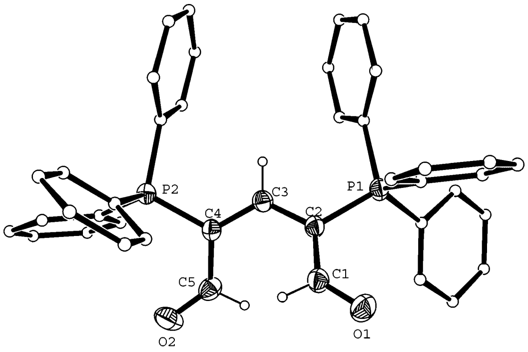


FIGURE 1. Molecular structure for the compound cation of **2**. The hydrogens of phenyls are omitted for clarity. Selected bond lengths [Å] and angles [deg]: O1−C1 1.211(3), C1−C2 1.429(4), C2−C3 1.383(4), C3−C4 1.379(3), C4−C5 1.425(4), O2−C5 1.208(3), C2−P1 1.761(3), C4−P2 1.750(3); O1−C1−C2 126.5(2), C1−C2−P1 116.8(2), C3−C2−P1 120.43(19), C3−C4−P2 120.3(2), C5−C4−P2 118.30(19), O2−C5−C4 125.8(3), C1−C2−C3 121.8(2), C2−C3−C4 124.7(2), C3−C4−C5 121.3(2).

The solid-state structure of **2** is fully supported by NMR spectroscopy and elemental analysis. The ^{31}P{^{1}H} NMR

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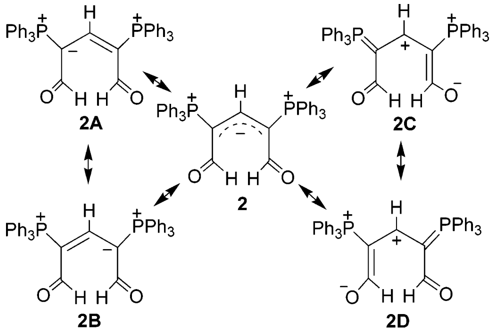
SCHEME 2. Resonance Structures for the Cation of 2



spectrum in CD_2Cl_2 showed only one C*P*Ph$_3$ signal at 23.38 ppm. The ^1H NMR spectrum in CD_2Cl_2 showed the characteristic C*H*O signal at 9.70 ppm and the C(PPh$_3$)C*H* at 6.71 ppm. The $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 showed the signals for *C*HO, *C*PPh$_3$, and C(PPh$_3$)*C*H at 185.3, 96.3, and 159.2 ppm, respectively. Compared to the value of the *C*H$_2$ signal in ethylene (123.3 ppm) and the *C*H signal in benzene (128.5 ppm),[4] the significantly upfield shift of *C*PPh$_3$ signal (96.3 ppm) indicates that the resonance structures **2A** and **2B** (Scheme 2) are the important contributors, whereas the $^{13}C\{^1H\}$ NMR chemical shift for C(PPh$_3$)*C*H signal (159.2 ppm) is obviously downfield, implying **2C** and **2D** (Scheme 2) are also the contributive resonance structures, which may mainly be attributed to the strong electron-withdrawing effect of the two phosphonium groups and the two carbonyl groups. In the IR spectrum of **2**, owing to the delocalized structure of the C_5 backbone, the C═O stretch vibration (1634 cm^{-1}) appeared at exceptionally low frequency.

As described above, compound **2** was synthesized in the presence of nitric acid. Compound **2** has remarkable anti-oxidative ability compared to most aldehydes that are easily oxidized. In addition, compound **2** is air-stable, and its thermal stability is also notable in that a solid sample remains virtually unchanged even when heated at 200 °C in air for 1 day. The high stability of compound **2** is probably related to the electronic effect of the two phosphonium groups and the protecting effect of the two bulky PPh$_3$ substituents. Furthermore, the resonance structures **2A**−**2D** (Scheme 2) may also contribute to the stability of **2**.[6]

To further confirm the anti-oxidative character of compound **2**, its electrochemical behaviors have been studied. Figure 2 shows the cyclic voltammetry (CV) of compound **2** recorded in $CH_2Cl_2+Bu_4NClO_4$ (0.1 M) using a glassy carbon disk working electrode in an undivided cell. In the positive scanning direction, the CV of **2** (Figure 2a) shows that there is no oxidation current in the potential window under +1.10 V, compared to the CV of the blank solution only containing CH_2Cl_2 and Bu_4NClO_4 (0.1 M) (Figure 2b). A quasi-reversible reduction process is observed, $E_{pc} = -1.71$ V and $E_{pa} = -1.50$ V (vs Ag/AgCl), $\Delta E_p = 210$ mV, when the scan rate is at 100 mV s^{-1}. The process exhibits a linear dependence of the cathodic peak current on the square root of the scan rate ($v^{1/2}$) from 20 to 200 mV s^{-1}, as expected for a diffusion controlled process (see Supporting Information). The CV results of the negative scan demonstrate that the electrochemical reduction process is followed by chemical reaction of the reduced intermediate, which implies an electrochemical (EC) mechanism.[7]

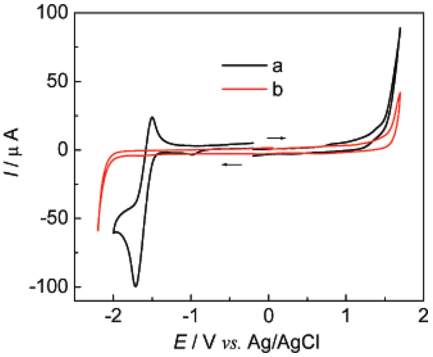
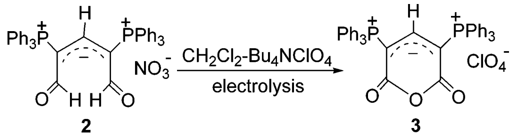


FIGURE 2. Cyclic voltammograms on a glassy carbon electrode at 100 mV s^{-1} of 6 mM compound **2** (a) and blank solution (b) (vs Ag/AgCl) in CH_2Cl_2 solution containing Bu_4NClO_4 (0.1 M).

SCHEME 3. Electrosynthesis of 3 from 2



In addition, controlled potential electrolysis was performed at 1.00 and 1.50 V (vs Ag/AgCl) in CH_2Cl_2 solution containing 0.1 M Bu_4NClO_4 in a divided electrochemical cell. When the current was close to zero, the electrolyte solution was evaporated to dryness under vacuum, and $^{31}P\{^1H\}$ and ^1H NMR data of the residue displayed that chemical shifts of the dialdehyde remained unchanged. The results of CV and electrolysis indicate that compound **2** has excellent electrochemically anti-oxidative ability. To further test the electrochemically anti-oxidative ability of **2**, controlled potential electrolysis was carried out at high electrolytic potential of 2.0 V (vs Ag/AgCl) in a divided electrochemical cell. The electrolysis was stopped when the current was negligible. NMR characterization of the electrolyte showed that complete transformation of **2** was achieved. Moreover, we obtained compound **3** in 53% yield by its isolation from the electrolyte (Scheme 3).

Unambiguous confirmation for the structure of **3** was determined by X-ray diffraction (Figure 3). The compound **3** contains a planar six-membered O-heterocycle with two PPh$_3$ substituents as reflected by the small deviations (0.0405 Å) from the rms planes of the best fit through the six atoms C1, C2, C3, C4, C5, and O2. The lack of significant alternation in the C−C bond distances within the heterocycle suggests that **3** has a delocalized structure.

Consistent with the solid-state structure, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed only one singlet at 21.01 ppm for C*P*Ph$_3$. The ^1H NMR spectrum in CD_2Cl_2 showed the signal for CPPh$_3$C*H* at 6.66 ppm. The $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 showed the signals for C(PPh$_3$)*C*O, *C*PPh$_3$, and CPPh$_3$*C*H at 163.0, 80.8, and 160.5 ppm, respectively. The IR spectrum

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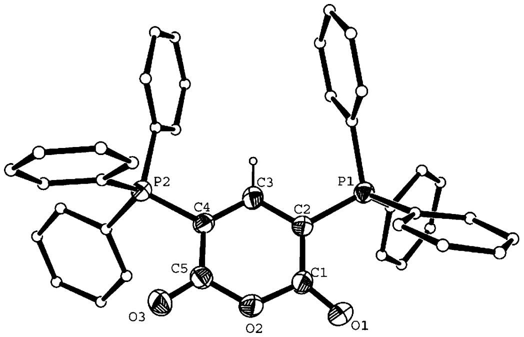

FIGURE 3. Molecular structure for the compound cation of **3**. The hydrogens of phenyls are omitted for clarity. Selected bond lengths [Å] and angles [deg]: O1−C1 1.210(3), O2−C1 1.397(3), C1−C2 1.432(3), C2−C3, 1.386(3), C3−C4 1.372(3), C4−C5 1.432(3), O2−C5 1.397(3), O3−C5 1.214(3), C2−P1 1.767(2), C4−P2 1.762(2); O1−C1−C2 128.1(2), O1−C1−O2 115.2(2), C1−C2−P1 118.98(18), C3−C2−P1 121.76(18), C3−C4−P2 123.97(19), C5−C4−P2 116.66(19), O3−C5−C4 126.6(2), O3−C5−O2 116.5(2), C1−C2−C3 119.3(2), C2−C3−C4 122.7(2), C3−C4−C5 119.2(2), C5−O2−C1 124.0(2).

displayed the absorption bands at 1719 and 1665 cm^{-1}, assigned to the C═O asymmetric and symmetic stretching modes respectively, were shifted toward anomalously low frequency, largely depending on the conjugated structure of the planar six-membered O-heterocycle.

Additionally, compound **3** is stable in water and also remains virtually unchanged when heated at 200 °C in air for 1 day. Like compound **2**, the electronic and protecting effect of two phosphonium groups may play an important role in the high stability of compound **3**.

In summary, we have synthesized and structurally characterized a novel dialdehyde that has remarkable thermal stability and oxidation resistance properties. This dialdehyde represents a rare example of an anti-oxidative aldehyde that is stable even in the presence of nitric acid. In addtion, the electrochemical properties of the dialdehyde have been studied by cyclic voltammetry, and a stable cyclic anhydride was obtained from the dialdehyde via an electrochemical method, which has attracted considerable attention as a green chemistry process.[8]

Experimental Section

Additional experimental details can be found in the Supporting Information.

[OHCC(PPh$_3$)CHC(PPh$_3$)CHO]NO$_3$(2). Concentrated nitric acid (65%, 0.6 mL, 8.8 mmol) was added to a solution of ruthenabenzene **1** (1.35 g, 1.0 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for about 5 h to give a brown solution, and then aqueous $NaHCO_3$ (0.5 M, 20 mL) was added to neutralize the solution. The resulting mixture was filtered to remove the solid suspension. The organic layer was separated and dried by $MgSO_4$. The volume of the organic layer was reduced to approximately 3 mL under vacuum. The residue was poured into ether (60 mL), and the precipitate was collected by filtration, washed with ether (5 × 10 mL), and dried in vacuo to give **2** as a light-yellow solid (0.63 g, 93%). IR (thin film, cm^{-1}): 3058, 2914, 2844, 2809, 2739, 1634, 1609, 1505, 1439, 1346, 1315, 1104, 719, 688. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ_H 6.71 (t, $J = 16.1$ Hz, 1H), 9.70 (d, $J = 21.6$ Hz, 2H), 7.66−7.36 (m, 30H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ_P 23.38 (s). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ_C 185.3 (d, $J = 5.4$ Hz), 159.2 (t, $J = 14.0$ Hz), 96.3 (dd, $J = 96.7$ Hz, $J = 15.1$ Hz), 134.4−119.0 (m). Anal. Calcd for compound **2**: C 72.24, H 4.88, N 2.05. Found: C 71.76, H 4.77, N 2.00.

[OC(O)C(PPh$_3$)CHC(PPh$_3$)C(O)]ClO$_4$ (3). A solution of compound **2** (0.48 g, 0.70 mmol) and Bu_4NClO_4 (0.68 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was oxidized at 2.0 V (vs Ag/AgCl) in a divided cell. The electrolysis was stopped when the current was negligible, and the solvent of the resulting mixture was removed completely under vacuum. The residue was washed with MeOH/H_2O 1:2 (5 × 10 mL) and dried under vacuum to give a brown solid (0.27 g, 53%). IR (thin film, cm^{-1}): 3050, 2918, 2867, 1719, 1665, 1533, 1439, 1085, 719, 688. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ_H 6.66 (t, $J = 13.5$ Hz, 1H), 7.78−7.35 (m, 30H). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ_P 21.01 (s). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ_C 163.0 (d, $J = 14.0$ Hz), 160.5 (t, $J = 13.1$ Hz), 80.8 (dd, $J = 118.4$ Hz, $J = 11.9$ Hz), 134.7−114.3 (m). Anal. Calcd for compound **3**: C 67.17, H 4.26. Found: C 67.29, H 4.57.

X-Ray Crystal Structure Determination of 2 and 3. Crystals of **2** and **3** suitable for X-ray diffraction were grown from CH_2Cl_2 solutions layered with diethyl ether. A light-yellow blocked crystal of **2** and an orange blocked crystal of **3** were mounted on top of glass fibers and transferred into a cold stream of nitrogen. Intensity data were collected on a Bruker Smart CCD Area Detector (**2**) and an Oxford Gemini S Ultra CCD Area Detector (**3**) respectively, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 223 K. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. Crystal data for **2**: $C_{41}H_{33}NO_5P_2$, $M_r = 681.62$, Triclinic, $P\bar{1}$, $Z = 2$, $a = 9.594(3)$ Å, $b = 10.695(4)$ Å, $c = 17.058(6)$ Å, $\alpha = 98.626(6)°$, $\beta = 95.024(6)°$, $\gamma = 108.664(6)°$, $V = 1622.2(9)$ Å^3; 11 756 reflections, 5649 independent reflections ($R_{int} = 0.0302$); $R_1 = 0.0561$, $wR_2 = 0.1619$ for 442 parameters and 4396 reflections with [$I > 2\sigma(I)$]. Crystal data for **3**: $C_{41}H_{31}ClO_7P_2$, $M_r = 733.05$, Monoclinic, $P2(1)/c$, $Z = 4$, $a = 16.8145(5)$ Å, $b = 12.2319(4)$ Å, $c = 17.1881(5)$ Å, $\alpha = 90°$, $\beta = 95.017(3)°$, $\gamma = 90°$, $V = 3521.59(19)$ Å^3; 17 829 reflections, 6182 independent reflections ($R_{int} = 0.0501$); $R_1 = 0.0399$, $wR_2 = 0.0649$ for 460 parameters and 3219 reflections with [$I > 2\sigma(I)$]. For further details on crystal structures, see the crystallographic information file in the Supporting Information.

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

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