

Keywords: antibiotics • autoxidation • cyclizations • Domino reactions • intermediates

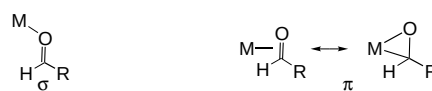
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Structure and Reactivity of a Cobalt(II) Phthalaldehyde Complex with Both σ - and π -Bonded Aldehyde Groups**

Christian P. Lenges, Maurice Brookhart,* and Peter S. White

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

The coordination of the carbonyl group of a ketone or aldehyde to a transition metal is of importance in metal-mediated catalysis and has been investigated in some detail. Aldehydes coordinate in a σ or π fashion, depending on the metal center, the oxidation state, the formal charge of the complex, and the steric requirements of the substrate or ancillary ligands (Scheme 1). In some cases an equilibrium



Scheme 1. Coordination modes of dialdehydes to transition metal complexes.

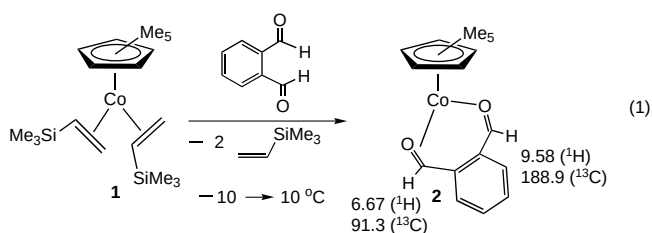
between the coordination modes is established.^[1–16] Here we describe the unique structure and reactivity of a Co^I phthalaldehyde complex in which both coordination modes are realized.

Cobalt aldehyde^[17, 18] complexes are quite rare, and transition metal complexes of dialdehydes such as phthalaldehyde are also uncommon.^[19, 20] Bosnich et al. reported^[19] the spectroscopic characterization of the cationic Rh^I phthalaldehyde complex $[\text{Rh}(\text{dcpe})\{\eta^1, \eta^2\text{-(C(O)H)}_2\text{C}_6\text{H}_4\}]^+$.^[21] This rhodium complex is stable only at low temperatures and undergoes catalytic formation of a five-membered lactone. The resting state of the catalyst in this process is unknown. The cobalt complex reported here is to our knowledge the first structurally characterized transition metal complex in which a dialdehyde exhibits both coordination modes in the same molecule. The complex is also the resting state in a catalytic intramolecular aldehyde condensation reaction (Tishchenko reaction)^[22–31] that generates a five-membered lactone.

Treatment of the labile Co^I bis-olefin complex **1**^[32] with phthalaldehyde according to equation (1) ($[\text{D}_6]$ acetone, -10°C , 10 equiv) resulted in a rapid color change from orange to dark green; NMR analysis showed complete substitution of coordinated olefin to generate a single new Co species after 10 min. One new C_5Me_5 signal was observed at $\delta = 1.70$ (s, 15 H) along with four resonances in the aromatic

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region for an unsymmetrically bound phthalaldehyde molecule at $\delta = 7.29, 7.62, 7.66$, and 8.09 . Most significant are two singlets for the aldehyde protons at $\delta = 6.67$ and 9.58 . The ^{13}C NMR spectrum (-10°C , $[\text{D}_6]\text{acetone}$) showed signals at $\delta = 91.3$ (d, $J_{\text{C,H}} = 173$ Hz) and 188.9 (d, $J_{\text{C,H}} = 188$ Hz) for the two differently coordinated carbonyl groups. Free phthalaldehyde has NMR signals for the equivalent aldehyde groups at $\delta = 10.52$ (^1H) and 192 (^{13}C) in $[\text{D}_6]\text{acetone}$. On the basis of this NMR evidence, **2** was formulated as a Co phthalaldehyde complex in which one aldehyde group is coordinated in a σ fashion and the other in a π fashion.

Attempts to isolate **2** by chromatography were unsuccessful, but **2** could be crystallized from acetone at -78°C after 3 d in moderate yield (32%). Black-green crystals were obtained which are air sensitive and decompose under ambient conditions in an inert atmosphere.

Complex **2** was characterized by single-crystal X-ray structure determination (Figure 1), which confirmed the proposed structure. The two aldehyde groups of a phthalaldehyde molecule are coordinated to the $(\text{C}_5\text{Me}_5)\text{Co}^{\text{I}}$ moiety to generate an

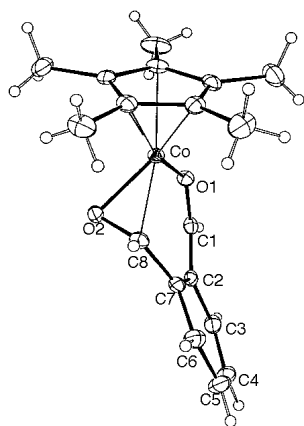


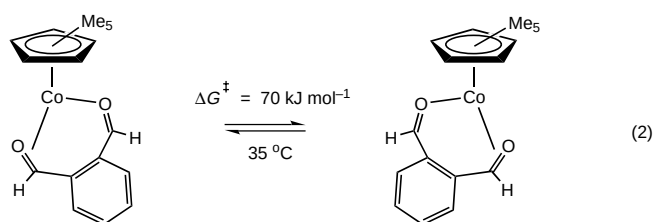
Figure 1. Crystal structure of **2** (ORTEP plot, 50% probability ellipsoids). Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Co–O1 1.8900(1), Co–O2 1.8932(10), Co–C8 2.0036(15), O1–C1 1.2590(19), O2–C8 1.3306(20), C1–C2 1.4305(22), C7–C8 1.4523(22), C2–C7 1.4192(22), C2–C3 1.4161(22), C3–C4 1.371(3), C4–C5 1.385(3), C5–C6 1.377(3), C6–C7 1.4034(23); O1–Co–O2 90.92(4), Co–O1–C1 128.66(10), O1–Co–C8 93.82(6), Co–O2–C8 39.80(6), O2–Co–C8 39.80(6), Co–C8–O2 65.62(8), O2–Co–O1–C1 39.64(14), C8–Co–O1–C1 0.10(14), C1–C2–C7–C8 23.61(16), O1–Co–C8–O2 86.85(17), C2–C3–C4–C5 1.39(17), C5–C6–C7–C2 6.64(18).

asymmetric, 18-electron cobalt(I) bis-aldehyde complex (only two oxygen atoms and one carbon atom of the aldehyde are within bonding distance to cobalt). The C=O bond lengths differ considerably: 1.26 $\text{\AA}$ for the σ -coordinated aldehyde (C1–O1) and 1.33 $\text{\AA}$ for the π -coordinated aldehyde (C8–O2) group. The elongated C=O bond of the π -coordinated aldehyde indicates considerable backbonding from a filled d orbital

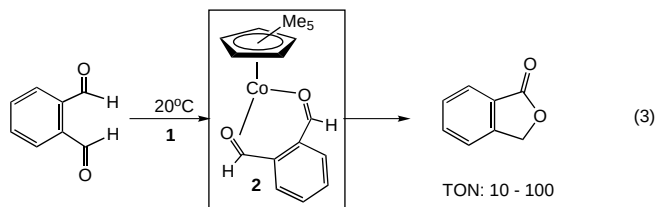
of the cobalt(I) center, thus reducing the C–O bond order. The structurally characterized nickel(0) benzaldehyde complex $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-C}_6\text{H}_5\text{CH=O})]$ ^[33–35] has a C=O bond length of $1.325(7)$ $\text{\AA}$ (^1H NMR: $\delta = 5.58$), which is similar to that of the π -coordinated aldehyde in **2**. The shorter C=O distance of the other aldehyde group is indicative of the greater double-bond character typical of a σ -bound aldehyde group. This bond length lies in the range reported for cationic and neutral Lewis acidic transition metal aldehyde adducts which bind aldehydes in a σ fashion.^[1–3, 6, 36–38] The two Co–O distances are quite similar (Co–O1 1.8900(1), Co–O2 1.8932(10) $\text{\AA}$). The Co–C1 distance is well outside bonding range (2.85 $\text{\AA}$), and the long Co–C8 bond (2.00 $\text{\AA}$) suggests that a change in coordination mode, which may be required for further reactions of this complex, might be initiated along this trajectory.

Coordination of phthalaldehyde to the Co center also clearly influences the bond lengths in the aromatic ring, which range from 1.42 $\text{\AA}$ (C2–C7) to 1.37 $\text{\AA}$ (C3–C4, C5–C6). The most significant influence of the transition metal on the conformation of phthalaldehyde is the C1–C2–C7–C8 torsion angle of 23° , which reflects the deviation from planarity of the aldehyde units upon coordination to the $(\text{C}_5\text{Me}_5)\text{Co}$ moiety. This leads to a C5–C6–C7–C2 torsion angle of 6.6° in the aromatic ring. The bond angles of the carbonyl groups to the aromatic ring are within the expected range (ca. 120°); however, the O1–Co–O2 angle is only 91° , which seems required to generate a favorable bonding interaction with both aldehyde groups. The O1–Co–C8–O2 torsion angle of 86° indicates that the σ -coordinated aldehyde group (C1–O1) is nearly parallel to the Co–C8 axis, and the angle between the coordination axes of the π - and σ -coordinated aldehyde groups is nearly 90° . This arrangement facilitates backbonding between d orbitals of cobalt and the σ -coordinated aldehyde group.

At -20°C the two aldehyde ^1H NMR signals are sharp singlets ($\nu_{1/2} = 1.5$ Hz). Warming the acetone solution results in line broadening of both peaks; this indicates a dynamic process which exchanges the sites of the π - and σ -coordinated aldehyde groups. Line-shape analysis of spectra obtained at different temperatures gave activation energies for this process of $\Delta G^\ddagger = 69$ kJ mol^{-1} ($k = 45$ s^{-1}) at 51°C , 70 kJ mol^{-1} (11 s^{-1}) at 35°C , and 68 kJ mol^{-1} (4.2 s^{-1}) at 21°C . Since the presence of excess phthalaldehyde had no influence on the line broadening, the process does not involve intermolecular exchange via free phthalaldehyde. Hence, this site exchange on the NMR time scale is attributed to a reversible interchange of σ and π coordination modes of the aldehyde groups. As indicated above, the long distance Co–C8 suggests the release of the π -coordinated aldehyde group and rotation of the $(\text{C}_5\text{Me}_5)\text{Co}$ moiety to generate a σ -bound aldehyde group and vice versa [Eq. (2)].



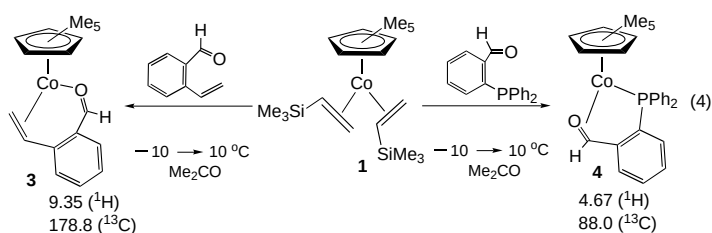
In the presence of excess phthalaldehyde, catalytic formation of the five-membered lactone occurs at 5 °C and above. Turnover numbers (TON) on the order of 100 were observed in the reaction of 1 mol % of **1** with phthalaldehyde. To obtain more detailed information, the reaction of 20 equivalents of phthalaldehyde with **1** at 20 °C was monitored by NMR spectroscopy. Complex **2** is generated rapidly in the initial phase of catalysis. After 9 h 50 % conversion to the lactone is observed in toluene, and after 24 h conversion of the aldehyde is complete [Eq. (3)]. In the initial stages of catalysis, **2** is the



only cobalt-containing species present; after 3 h other organometallic cobalt complexes had been formed, and after complete conversion a variety of unidentified cobalt complexes were observed, which primarily arise from decarbonylation reactions.^[39] This suggests that the rate of lactonization is independent of aldehyde concentration and that the intramolecular cyclization is the slow step in this process.

With simple aldehydes **1** undergoes oxidative addition reactions to generate cobalt(III) acyl hydride complexes, which are intermediates in catalytic hydroacylation.^[40] In the presence of an excess of various alkyl aldehydes, catalytic dimerization to give the Tishchenko esters was observed. This suggests that the intramolecular Tishchenko reaction also follows a pathway that is initiated by oxidative addition of the aldehyde. This mechanistic scenario was also proposed by Bosnich et al. for cationic rhodium bis-phosphane complexes as catalysts.^[19]

It is informative to compare compound **2** with other Co^I aldehyde complexes. We previously reported the synthesis of the chelated aldehyde olefin complex **3**^[32] [Eq. (4)] by



reaction of **1** with *o*-formylstyrene. The NMR data for the aldehyde group of **3** suggest σ coordination. However in complex **4**, which was prepared quantitatively in an analogous fashion by adding a stoichiometric amount of *o*-diphenylphosphanylbenzaldehyde to a solution of **1** in acetone, the aldehyde coordinates in a π fashion to the cobalt center, as suggested by the ¹H NMR signal [Eq. (4)]. In these cases the ambivalent nature of the carbonyl group allows σ or π coordination, depending on the bonding mode of the other ligated group of the bidentate ligand. In **3** the olefin can only bind in a π -fashion; its significant π acidity removes electron

density from the Co^I center and thus favors σ binding of the aldehyde by interaction with the lone pair of electrons of the carbonyl group. In complex **4**, the PPh₂ group binds predominantly by a σ -donor interaction, and the higher electron density at the Co^I center favors binding of the aldehyde in a π fashion with significant backbonding from cobalt to the π^* orbital of the carbonyl group. On the basis of the behavior of complexes **3** and **4**, it is easy to rationalize why the dialdehyde complex **2** prefers to bind through one σ and one π interaction.

Experimental Section

All operations were carried out under an argon atmosphere. All solvents were degassed and purified by standard methods.

2: Five equivalents of phthalaldehyde were added to a solution of **1** (0.15 g, 0.38 mmol) in acetone (5 mL) at 0 °C. The mixture was stirred for 1 h at this temperature during which time the color changed to dark green. Cooling to -78 °C resulted in the deposition of black-green crystals, which were isolated by filtration and stored at -20 °C in a dry-box freezer (yield: 0.04 g, 0.12 mmol, 32 %). The material obtained in this way was suitable for X-ray structure analysis. ¹H NMR (300 MHz, [D₆]acetone, -10 °C): δ = 1.70 (s, 15H; C₅Me₅), 6.67 (s, 1H; π -C(O)H), 7.29, 7.62–7.66, 8.09 (m, 4H; ArH), 9.58 (s, 1H; σ -C(O)H); ¹³C{¹H} NMR: δ = 8.6 (C₅Me₅), 88.6 (C₅Me₅), 91.3 (d, J = 173 Hz; π -C(O)H), 188.9 (d, J = 188.2 Hz; σ -C(O)H), 123.4, 125.6, 126.7, 131.2, 133.5, 143.6 (Ar).

Crystal structure data for **2**: C₁₈H₂₁O₂Co, M_r = 328.29, monoclinic, space group $P2_1/n$, Z = 4, a = 10.1111(5), b = 8.7370(4), c = 17.4463(8) Å, β = 96.1400(10)°, V = 1532.38(12) Å³, ρ_{calc} = 1.423 g cm⁻³, T = -110 °C, $2\theta_{\text{max}}$ = 60°, MoK α radiation (λ = 0.71073 Å); 20178 reflections were measured, 4435 unique reflections were obtained, and 3914 of these with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Siemens SMART diffractometer by the omega scan method. For significant reflections $R(\text{merge})$ = 0.022; residuals: R_F = 0.032, R_w = 0.037 (significant reflections), GOF = 3.11.^[41]

4: To a stirred solution of **1** (0.15 g, 0.38 mmol) in acetone was added one equivalent of *o*-diphenylphosphanylbenzaldehyde at 20 °C. An immediate color change from red to brown was observed, and stirring was continued for 30 min. Removal of all volatile materials left **4** as a brown oil (0.18 g, 0.38 mmol). ¹H NMR (300 MHz, [D₆]acetone, -10 °C): δ = 1.49 (s, 15H; C₅Me₅), 4.67 (s, 1H; C(O)H), 7.05–7.19 (m, 3H; ArH), 7.36–7.45 (m, 6H; ArH), 7.52 (m, 4H; ArH), 8.33 (m, 1H; ArH); ¹³C{¹H} NMR: δ = 9.61 (C₅Me₅), 88.01 (d, 168.6 Hz, C(O)H), 90.80 (C₅Me₅), 124.1, 126.6, 128.8, 129.9, 130.1, 133.3, 135.0, 133.2, 137.2, 159.5 (Ar); ³¹P{¹H} NMR: δ = 58.1 (br).

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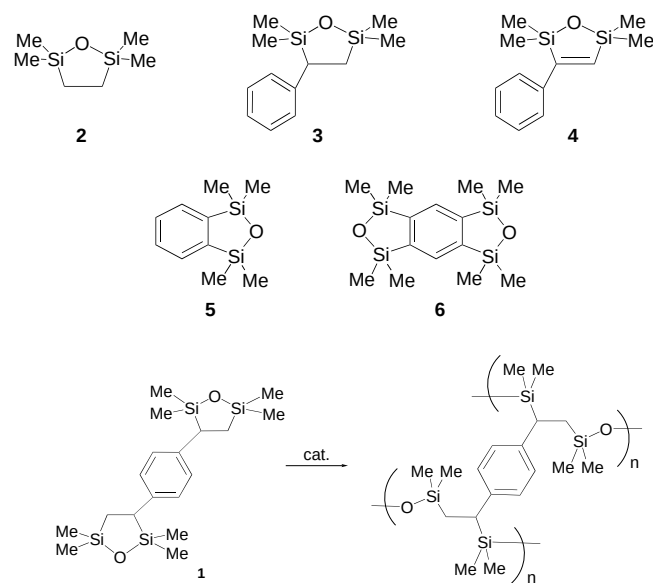
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Phenylene-Bridged Cyclic Siloxanes as Precursors to Nonshrinking Sol–Gel Systems and Their Use as Encapsulants

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Sol–gel polymerization has been the focus of much attention in the design and preparation of highly cross-linked polysiloxane gels.^[1, 2] However, application of sol–gel systems has been limited by the shrinkage associated with the evaporation of the solvent needed for monomer/water miscibility and the resulting condensation products formed during polymerization. An attractive strategy for reducing shrinkage is to eliminate solvent^[3] and condensation by-products entirely by replacing the step-growth polymerization used in the sol–gel processing of alkoxy silanes with a chain-growth polymerization, such as ring-opening polymerization (ROP). ROP is a chain-growth process that has proven to be an effective means for reducing or, as with the polymerization of spiroorthocarbonates, completely eliminating shrinkage in linear, hydrocarbon polymers.^[4] In this study, we have prepared a new class of sol–gel processed, hybrid organic–inorganic materials based on the ROP of monomers **1–3** bearing one or more 2,2,5,5-tetramethyl-2,5-disilaoxacyclopentane groups (Scheme 1).



Scheme 1. Ring-opening polymerization of **1** to the corresponding polymer.

Unlike the sol–gel chemistry of alkoxy silanes, which requires stoichiometric quantities of water, ROP of disilaoxacyclopentane groups only requires catalytic quantities of an anionic base, such as tetrabutylammonium hydroxide

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