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Note

Synthesis and Reactivity of Five-Membered Palladalactones from Arylallenes and Carbon Dioxide: Relevance to Catalytic Lactone Synthesis

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Supporting Information

ABSTRACT: A bis(tri-*n*-butylphosphine)palladium $((nBu_3P)_2Pd)$ complex was shown to catalyze the cyclization of arylallenes with carbon dioxide to yield six-membered lactones. The stoichiometric reaction of a $(Me_3P)_2Pd$ complex with 1 equiv of arylallenes, followed by treatment with CO₂, resulted in the formation of five-membered palladalactones,



the structures of which were fully characterized by X-ray crystallography, NMR, IR, HRMS, and elemental analysis.

igcap ynthetic chemists have long dreamed of using carbon O dioxide as a starting material for chemical syntheses. Carbon-carbon bond formation using CO₂ is both particularly attractive and challenging.¹ Although Ni- or Pd-catalyzed sixmembered lactone syntheses from butadienes and acetylenes have been well-documented,² few examples of reactions between CO₂ and allenes have been reported.³ The lactones obtained from these reactions have been used in a variety of reactions, including hydrogenation, hydroformylation, hydroaminomethylation, hydroamination, alcoholysis, hydration, hydrosilation, oxidation, and polymerization reactions.⁴ Sasaki reported a low yield for the Ni-catalyzed reaction of unsubstituted allene and CO_2 .^{3b} Tsuda et al. obtained lactones in a moderate yield for a specific substrate (methoxyallene) using a palladium catalyst coordinated by P-N ligands or Cy₃P.^{3c} Mechanistic investigations of these systems have not yet been conducted. We report here the preparation of sixmembered lactones from arylallenes and CO₂ in the presence of (nBu₃P)₂Pd catalysts. We identified several possible catalytic intermediates on the basis of the results obtained from the stoichiometric reactions.

RESULTS AND DISCUSSION

Catalytic Reaction. Phenylallene reacted with CO_2 (50 bar) at 80 °C in the presence of a catalytic amount of a $(nBu_3P)_2Pd$ complex to yield a set of six-membered lactones, with 3,5-dibenzyl-2-pyrone (A) as the major isomer, in a moderate yield (eq 1). The use of other phosphine ligands,



such as Me₃P, tBu₃P, Cy₃P, Ph₃P, and Ph₂CH₂CH₂PPh₂, resulted in poor yields. The lactone produced contained isomeric products at each C=C double bond, although the selectivity for the production of lactone **A** was 80%.⁵ Higher pressures and lower temperatures decreased the selectivity of **A**. The reaction of 3-phenyl-1-propyne with CO₂ in the presence of a catalytic amount of $(nBu_3P)_2Pd$ complex did not give **A**. The reaction path via the isomerization of phenylallene to the corresponding acetylene was negligible under the present reaction conditions.

Stoichiometric Reaction. A possible mechanism for the lactone synthesis is shown in Scheme 1. The thermolysis of $(\eta^5$ - C_5H_5)Pd(η^3 - C_3H_5), a convenient precursor for palladium(0), in the presence of 1 equiv of arylallene resulted in the generation of a new complex assignable to $(Me_3P)_2Pd(\eta^2$ - $CH_2 = C = CHAr)$ (2a, Ar = C_6H_5 ; 2b, Ar = $C_6H_4OCH_3$ -p). A large high-field shift in the C=CH₂ ¹H NMR signal, to δ 2.66 ppm, strongly supported the formation of a coordination complex with palladium. The arylallene appeared to be horizontally oriented and coplanar with the P-Pd-P plane, because the two phosphorus atoms were not equivalent, according to the ${}^{31}P{}^{1}H{}^{1}$ NMR spectrum. On the other hand, the reaction of Pd(0) with excess arylallene resulted in a new complex assignable to palladacyclopentane (3). The formation of a similar metallacyclopentane was reported in the context of reactions of allenes with transition-metal complexes.⁶

Figure 1 shows the molecular structure of 3a, which assumed a square-planar coordination geometry around the Pd center such that the two PMe₃ ligands were located at the cis positions. The C–C bond lengths in the five-membered chelated ring (C4–C5 = 1.490(2) Å, C5–C5* = 1.484(3) Å) were similar to the bond length (1.49(2) Å) reported previously for rhodacyclopentane, which was prepared by the

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Scheme 1. Possible Mechanism for the Formation of A





Figure 1. ORTEP drawing of palladacyclopentane **3a**. Hydrogen atoms are omitted for simplicity; thermal ellipsoids are drawn at the 50% probability level. Atoms with asterisks are crystallographically equivalent to the atoms labeled with the same number without asterisks. Selected bond lengths (Å) and angles (deg): Pd1–P1 = 2.3200(5), Pd1–C4 = 2.0973(16), C4–C5 = 1.490(2), C5–C5* = 1.484(3), C5–C6 = 1.355(3); P1–Pd1–P1* = 97.27(2), Pl–Pd1–C4 = 90.25(5), Pl–Pd1–C4* = 171.77(5), C4–Pd1–C4* = 82.45(9), Pd–C4–C5 = 110.19(11), C4–C5–C6 = 128.73(16), C4–C5–C5* = 111.37(11).

reaction of RhCl(PMe₃)₃ with arylallenes.^{6c} The single ³¹P{¹H} NMR signal at δ –21.95 ppm indicated a symmetrical structure. Complex **3b** yielded NMR spectra similar to those obtained from **3a** and was proposed to assume the same five-membered palladacycle structure.

Treatment of the $(Me_3P)_2Pd(\eta^2-CH_2=C=CHAr)$ complex (2) with CO₂ instantaneously resulted in the generation of a five-membered palladalactone (4). This is the first reported isolation of a CO₂-derived palladalactone. The structure was fully elucidated by elemental analysis, IR, ¹H NMR, ¹³C{¹H} NMR, and ³¹P{¹H} NMR. Figure 2 shows the X-ray crystal structures of **4a,b**, which were similar, as expected. The Pd center assumed a square-planar coordination geometry in which the two PMe₃ groups were located at the cis positions. The much shorter Pd1–P2 bond lengths (2.2262(3) Å (**4a**), 2.2211(17) Å (**4b**)) in comparison to the Pd1–P1 bond length (2.3448(4) Å (**4a**), 2.3470(17) Å (**4b**)) most likely arose from the influence of a Pd1–O1 bond in the trans position. The Pd1–C7 bond length (2.0662(13) Å (**4a**), 2.067(6) Å (**4b**)) was slightly shorter than the bond length (2.086(2) Å) reported previously for a palladalactone prepared by the reaction of (Me₃P)₂Pd(styrene) with diketene.⁷ Although the closely related nickelalactone was reported to form from allene and CO₂, the structure was proposed only on the basis of IR and elemental analysis.⁸

The six-membered lactones (A) were presumably produced through reductive elimination from the seven-membered palladalactone (5) formed via 3 or 4. The acetylene insertion into the five-membered nickelalactone was reported in the context of a six-membered lactone synthesis from 2 mol of acetylene and CO_2 .⁹ The formation of 5 through 4 was consistent with the regioselectivity of the catalytic reaction, which yielded the 3,5-disubstituted 2-pyrones.

In summary, we have demonstrated that $(nBu_3P)_2Pd$ complexes catalyze the cyclization between arylallenes and carbon dioxide to yield six-membered lactones. The catalysis presumably proceeds via the five-membered palladalactones, which are isolable from a stoichiometric reaction of $(Me_3P)_2Pd$, arylallene, and CO_2 .

EXPERIMENTAL SECTION

General Procedures. All manipulations of air-sensitive materials were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were purified by conventional means and were distilled immediately prior to use. $(\eta^5-C_5H_5)Pd(\eta^3 C_3H_5$) was synthesized according to the literature method.¹⁰ The ¹H, ¹³C¹H, and ³¹P¹H NMR spectra were recorded on a JEOL-LA400WB superconducting high-resolution spectrometer (400 MHz for $^1\text{H}).$ $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external 85% phosphoric acid. IR spectra were recorded on a Shimadzu FTIR-8500 spectrometer. The elemental analyses were carried out using a CE-EA 1110 automatic elemental analyzer. Reaction mixtures were analyzed by GC using GL Science TC-1 (60 m) capillary columns on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID). GC-MS data were obtained using a Shimadzu GC-17A gas chromatograph connected to a GCMS-QP 5000 mass spectrometer.

Preparation of 3,5-Dibenzyl-2-pyrone (A). In a stainless steel autoclave (20 cm³ inner volume), carbon dioxide (10 bar) was added to a mixture of CH₃CN (5 mL), (η^{5} -C₅H₅)Pd(η^{3} -C₃H₅) (47 mg, 0.22

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Figure 2. (a) ORTEP drawing of palladalactone **4a**. Hydrogen atoms are omitted for simplicity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd1–P1 = 2.3448(4), Pd1–P2 = 2.2262(3), Pd1–O1 = 2.0742(9), Pd1–C7 = 2.0662(13), O1–C9 = 1.2991(17), O2–C9 = 1.2329(17), C7–C8 = 1.5005(18), C8–C9 = 1.5146(18), C8–C10 = 1.342(2); P1–Pd1–P2 = 101.948(13), Pl–Pd1–O1 = 84.15(3), Pl–Pd1–C7 = 166.75(4), P2–Pd1–O1 = 172.60(3), P2–Pd1–C7 = 91.29(4), O1–Pd1–C7 = 82.70(5), Pd1–O1–C9 = 114.94(8), Pd1–C7–C8 = 106.06(9), O1–C9–O2 = 122.87(13), O1–C9–C8 = 114.89(11), O2–C9–C8 = 122.24(12), C7–C8–C9 = 116.23(12), C7–C8–C10 = 126.30(12), C9–C8–C10 = 117.21(12). (b) ORTEP drawing of palladalactone **4b**. Hydrogen atoms are omitted for simplicity; thermal ellipsoids are drawn at the 50% probability level. One of the two crystallographically independent molecules is shown. Selected bond lengths (Å) and angles (deg): Pd1–P1 = 2.3470(17), Pd1–P2 = 2.2211(17), Pd1–O1 = 2.091(4), Pd1–C7 = 2.067(6), O1–C9 = 1.262(7), O2–C9 = 1.293(7), C7–C8 = 1.443(8), C8–C9 = 1.473(7), C8–C10 = 1.403(7); P1–Pd1–P2 = 99.18(6), Pl–Pd1–O1 = 91.64(13), Pl–Pd1–C7 = 171.08(17), P2–Pd1–O1 = 168.92(13), P2–Pd1–C7 = 87.39(17), O1–Pd1–C7 = 82.1(2), Pd1–O1–C9 = 110.8(3), Pd1–C7–C8 = 103.3(4), O1–C9–O2 = 120.2(5), O1–C9–C8 = 118.1(5), O2–C9–C8 = 121.7(5), C7–C8–C9 = 114.1(5), C7–C8–C10 = 128.2(5), C9–C8–C10 = 116.5(5).

mmol), tri-*n*-butylphosphine (89 mg, 0.44 mmol), sodium acetate (AcONa) (18 mg, 0.22 mmol), and phenylallene (0.50 g, 4.30 mmol) at room temperature. The initial pressure was adjusted to 50 bar at 80 °C, and the autoclave was heated at that temperature for 12 h. After cooling, biphenyl (50 mg) was added to the reaction mixture as an internal standard for the GC analysis. The yield of 3,5-dibenzyl-2-pyrone (A) was determined by GC (0.45 g (38%), TON = 7.4). 3,5-Dibenzyl-2-pyrone (A) was purified using a Japan Analytical Industry Co. Lc-250HS recycling preparative HPLC. ¹H NMR (400 MHz in acetone- d_6): δ 3.68 (s, 2H, C_6H_5 -CH₂), 3.72 (s, 2H, C_6H_5 -CH₂), 7.03 (s, 1H), 7.12–7.36 (m, 10H, Ph), 7.46 (s, 1H). ¹³C{¹H} NMR (100 MHz in acetone- d_6): δ 35.53, 37.01, 119.63, 127.19, 127.36, 129.17, 129.42, 129.48, 129.58, 129.74, 139.45, 139.93, 142.37, 147.62, 162.52 (CO). IR (KBr, cm⁻¹): 1714 (ν (CO)). HRMS (FAB): calcd for C₁₉H₁₆O₂ (MH⁺) 276.1150, found 276.1151.

Preparation of 2a,b. A mixture of $(\eta^5-C_5H_5)Pd(\eta^3-C_3H_5)$ (0.51g, 2.40 mmol) and trimethylphosphine (0.37 g, 4.80 mmol) in diethyl ether (25 mL) was stirred for 0.5 h at room temperature. To the mixture were added diethyl ether (5 mL) and phenylallene (0.28 g, 2.40 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 3 h under an argon atmosphere. Removing the volatiles under vacuum and washing the residual solid with hexane $(3 \times 3 \text{ mL})$ gave 2a (0.70 g, 78% yield) as a yellow powder. This powder was used without further purification (97% purity, as determined by ¹H NMR). ¹H NMR (400 MHz in toluene d_8): δ 1.09 (br, 18H, P(CH_3)_3), 2.64 (br, 2H, CH_2=), 6.85 (br, 1H, =CH-), 7.10, 7.33, 7.89 (br, 5H, C_6H_5 -). ³¹P{¹H} NMR (160 MHz in toluene- d_8): $\delta - 27.1$ (br), -24.0 (br). ¹H NMR (400 MHz in THF d_8): δ 1.23 (br, 18H, P(CH₃)₃), 2.18 (br, 2H, CH₂=), 6.34 (br, 1H, =CH-), 6.87 (1H, para), 7.07 (2H, meta), 7.42 (2H, ortho). ³¹P{¹H} NMR (160 MHz in THF- d_8): δ –28.1 (br), –24.6 (br). ¹H NMR

(400 MHz in THF- d_8 at -60 °C): δ 1.24 (d, 9H, J(PH) = 7 Hz, P(CH₃)₃), 1.27 (d, 9H, J(PH) = 7 Hz, P(CH₃)₃), 2.10 (m, 2H, CH₂==), 6.36 (m, 1H, =CH-), 6.91 (1H, para), 7.11 (2H, meta), 7.47 (2H, ortho). ³¹P{¹H} NMR (160 MHz in THF- d_8 at -60 °C): δ -26.8 (d, J(PP) = 28 Hz), -23.6 (d, J(PP) = 28 Hz).

Complex **2b** was prepared analogously (85% yield) as a yellow powder. This powder was used without further purification (95% purity, as determined by ¹H NMR). ¹H NMR (400 MHz in toluened₈): δ 1.10 (br, 18H, P(CH₃)₃), 2.66 (br, 2H, CH₂=), 3.41 (s, 3H, -OCH₃), 6.84 (br, 1H, =CH-), 6.91 (1H, meta), 7.84 (2H, ortho). ³¹P{¹H} NMR (160 MHz in toluene-d₈): δ -27.2 (br), -23.9 (br).

Preparation of 3a,b. A mixture of (η^{5} -C₃H₅)Pd(η^{3} -C₃H₅) (0.17g, 0.80 mmol) and trimethylphosphine (0.13 g, 1.68 mmol) in THF (10 mL) was stirred for 0.5 h at room temperature. To the mixture was added phenylallene (0.37g, 3.20 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 24 h under an argon atmosphere. Volatiles were removed under vacuum, and the residual solid was washed with hexane (3 × 4 mL) and dried in vacuo. Recrystallization from toluene–hexane afforded **3a** as pale yellow crystals (0.25 g, 64%). ¹H NMR (400 MHz in CD₂Cl₂): δ 1.31 (d, 18H, *J*(PH) = 7 Hz, P(CH₃)₃), 2.33 (m, 4H, CH₂–), 6.05 (s, 2H, = CH–), 7.09 (2H, para), 7.27 (4H, meta), 7.49 (4H, ortho). ³¹P{¹H} NMR (160 MHz in CD₂Cl₂): δ –21.95. Anal. Calcd for C₂₄H₃₄P₂Pd: C, 58.72; H, 6.98. Found: C, 59.06; H, 6.71. Mp: 141–143 °C dec.

Complex **3b** was prepared analogously (50% yield) as colorless crystals. ¹H NMR (400 MHz in toluene- d_8): δ 0.80 (d, 18H, *J*(PH) = 7 Hz, P(CH₃)₃), 2.72 (br, 4H, CH₂-), 3.40 (s, 3H, -OCH₃), 6.64 (s, 2H, =CH-), 6.88 (4H, *meta*), 7.68 (2H, *ortho*). ³¹P{¹H} NMR (160 MHz in toluene- d_8): δ -22.30.

Preparation of 4a,b. An excess amount of CO_2 (0.19 g, 4.28 mmol) was vacuum-transferred into a diethyl ether (5 mL) solution of

2a (0.40 g, 1.07 mmol), and the mixture was stirred for 12 h at room temperature. The resulting solid product was collected by filtration, washed with hexane, and dried in vacuo. Recrystallization from CH₂Cl₂-THF gave 4a as colorless crystals (0.36 g, 80%). ¹H NMR (400 MHz in CD₂Cl₂): δ 1.31 (d, 9H, J(PH) = 9 Hz, $P(CH_3)_3$), 1.33 (d, 9H, J(PH) = 9 Hz, $P(CH_3)_3$), 2.53 (br, 2H, CH_2 -), 6.89 (br, 1H, =CH-), 7.13 (1H, para), 7.23 (2H, meta), 7.37 (2H, ortho). ¹³C{¹H} NMR (100 MHz in CD₂Cl₂): δ 14.54 (d, J(CP) = 21 Hz, $P(CH_3)_3$), 16.76 (d, J(CP) = 33 Hz, $P(CH_3)_3$), 29.64 (br, CH_2 -), 124.64 (br, -C=CH), 126.07, 127.75, 128.84, 138.01, 143.04 (br, -C=CH), 180.40 (CO). ${}^{31}P{}^{1}H{}$ NMR (160 MHz in CD₂Cl₂): δ -18.93 (d, J(PP) = 42 Hz), -5.11 (d, J(PP) = 42 Hz). IR (KBr, cm⁻¹): 1629 (ν (CO)). Anal. Calcd for C₁₆H₂₆O₂P₂Pd: C, 45.89; H, 6.26. Found: C, 45.59; H, 6.00. Mp 164-165 °C dec.

Complex 4b was prepared analogously (85% yield) as pale yellow crystals. ¹H NMR (400 MHz in CD_2Cl_2): δ 1.35 (d, 9H, J(PH) = 9 Hz, $P(CH_3)_3$, 1.40 (d, 9H, J(PH) = 9 Hz, $P(CH_3)_3$), 2.58 (br, 2H, CH_2 -), 3.77 (s, 3H, $-OCH_3$), 6.84 (d, 2H, J(HH) = 8 Hz, meta), 6.91 (br, 1H, =CH-), 7.40 (d, 2H, J(HH) = 8 Hz, ortho). ¹³C{¹H} NMR (100 MHz in CD_2Cl_2): δ 14.49 (d, J(CP) = 20 Hz, $P(CH_3)_3$), 16.65 $(d, I(CP) = 32 Hz, P(CH_3)_3), 29.21 (CH_2-), 55.76 (-OCH_3), 113.15$ (meta), 125.10 (-C=CH), 131.14 (ortho), 130.38 (ipso), 140.88 (-C=CH), 157.95 (para), 180.53 (CO). ³¹P{¹H} NMR (160 MHz in CD_2Cl_2 : δ -9.09 (d, J(PP) = 39 Hz), -5.26 (d, J(PP) = 39 Hz). IR (KBr, cm⁻¹): 1610 (ν (CO)). Anal. Calcd for C₁₇H₂₈O₃P₂Pd: C, 45.50; H, 6.29. Found: C, 45.38; H, 6.04. Mp 142 °C dec.

Crystal Structure Determination. Data collection was performed on a Bruker SMART APEX-II CCD diffractometer (Mo Ka radiation, graphite monochromator). The crystal data, data collection, and refinement parameters are summarized in Table S1 (Supporting Information). The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 using the SHELX-97 program.¹ Hydrogen atoms on carbon were included in the calculated positions.

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files giving NMR spectra of A and crystallographic data for 3a and 4a,b. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Aresta, M.; Dibenedetto, A. Dalton Trans. 2007, 2975. (b) Sakakura, T.; Choi, J.-C.; Yasuda, H. Chem. Rev. 2007, 107, 2365. (c) Omae, I. Coord. Chem. Rev. 2012, 256, 1384.

(2) (a) Carbon Dioxide as a Source of Carbon: Biochemical and Chemical Uses; Aresta, M., Forti, G., Eds.; ; D. Reidel: Dordrecht, The Netherlands, 1987. (b) Carbon Dioxide Activation by Metal Complexes; Weller, M. G., Ed.; Wiley-Interscience VCH: Weinheim, Germany, 1988

(3) (a) Döhring, A.; Jolly, P. W. Tetrahedron Lett. 1980, 21, 3201. (b) Sasaki, Y. J. Mol. Catal. 1989, 54, L9. (c) Tsuda, T.; Yamamoto, T.; Saegusa, T. J. Organomet. Chem. 1992, 429, C46. (d) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. Chem. Rev. 2000, 100, 3067.

(4) Behr, A.; Henze, G. Green Chem. 2011, 13, 25.

(5) See the Supporting Information for more details concerning structural identification of lactone A.

(6) (a) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1978, 1839. (b) Winchester, W. R.; Gawron, M.; Palenik, G. J.; Jones, W. M. Organometallics 1985, 4, 1894. (c) Choi, J.-C.; Sarai, S.; Koizumi, T.; Osakada, K.; Yamamoto, T. Organometallics 1998, 17, 2037.

(7) (a) Osakada, K.; Doh, M.-K.; Ozawa, F.; Yamamoto, A. Organometallics 1990, 9, 2197. (b) Kakino, R.; Nagayama, K.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. Chem. Lett. 1999, 685.

(8) Hoberg, H.; Oster, B. W. J. Organomet. Chem. 1984, 266, 321.

(9) (a) Hoberg, H.; Schaefer, D. J. Organomet. Chem. 1982, 238, 383. (b) Hoberg, H.; Schaefer, D.; Bruckhart, G.; Krüger, C.; Romão, M. J. I. Organomet. Chem. 1984, 266, 203.

(10) Tatsuno, Y.; Yoshida, T.; Otsuka, S. Inorg. Synth. 1979, 19, 220. (11) Sheldrick, G. M. SHELXL-97, Program for the Solution and the Refinement of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1997.