Organometallics **1994,** *13,* 407–409 407

Synthesis of the First Carbon Dioxide Coordinated Palladium(0) Complex, Pd(η^2-CO_2)($PMePh_2$)$_2$

Masato Sakamoto, Isao Shimizu,* and Akio Yamamoto*

Department of Applied Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

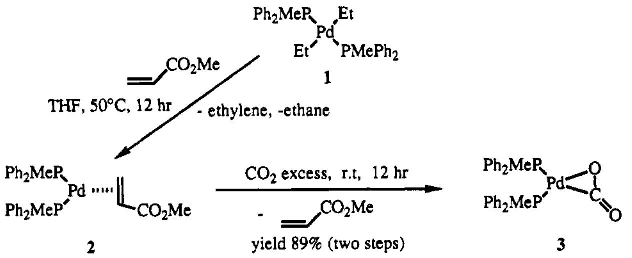
Received September 21, 1993[⊗]

*Summary: A new palladium(0) complex, (η^2-carbon dioxide)bis(methyldiphenylphosphine)palladium(0) (Pd(CO_2)($PMePh_2$)$_2$; **3**), has been prepared by the reaction of $PdEt_2(PMePh_2)_2$ (**1**) with methyl acrylate followed by treatment with CO_2. The complex was characterized by means of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy and the chemical reactions. Spectroscopic evidence indicates that complex **3** has a side-on (η^2) coordination mode. Thermal decomposition of the solution of complex **3** caused cleavage of the Pd-coordinated CO_2 to give CO and O=$PMePh_2$, together with CO_2. Hydrogenation of **3** yielded HCO_2H. Catalytic conversion of H_2 and CO_2 into formic acid was found to be promoted by $PdCl_2L_2$ (L = PMe_3, $PMePh_2$, PPh_3).*

Considerable attention has recently been paid to development of a new method to utilize carbon dioxide as a carbon source for organic synthesis.[1] Various types of CO_2-coordinated transition-metal complexes have been isolated and their structures characterized.[2] However, no report has been made on preparation of a CO_2-coordinated palladium complex in spite of the usefulness of palladium complexes in various organic syntheses[3] and of their potential utility in future development for CO_2 fixation with a palladium complex.

We now report the synthesis of a new CO_2-coordinated palladium complex and on the bonding mode of CO_2 with palladium. The complex was prepared as shown in Scheme 1 from diethylbis(tertiary phosphine)palladium (1) by treatment with methyl acrylate[4a] first, followed by reaction with CO_2 under pressure as shown by the following procedure (Scheme 1).

Scheme 1



To a solution of *trans*-$PdEt_2(PMePh_2)$ (1; 152.9 mg, 0.271 mmol, 1.00 equiv) in 1.2 mL of THF was added a slight excess of methyl acrylate (36.5 μL, 0.451 mmol, 1.50 equiv). The resulting mixture was stirred at 50 °C for 12 h to give the methyl acrylate coordinated palladium(0) complex 2 in situ. The solution was then treated with CO_2 (18–20 atm, 70–90 equiv) at room temperature to yield a yellow powder or microcrystalline solid of complex 3 (133.3 mg, yield 89%). Complex 3 is air sensitive and thermally unstable in the absence of CO_2; hence, it should be stored at −30 °C under CO_2.

The characteristic IR bands (KBr disk) due to the coordinated CO_2 ligand in 3 are observed at 1658 (vs) and 1634 cm^{-1} (vs) (ν(C=O)). These absorptions are very similar to those of the reported carbon dioxide coordinated nickel(0) complexes $Ni(CO_2)(PEt_3)_2$ (1660 (vs), 1635 cm^{-1} (vs)) and $Ni(CO_2)(P^nBu_3)_2$ (1660 (vs), 1632 cm^{-1} (vs)).[5] The ^1H NMR spectrum (90 MHz at −30 °C, in CD_2Cl_2) of 3 shows two doublets (δ 1.6 ppm, J = 10.8 Hz and δ 1.8 ppm, J = 11.0 Hz, 2PCH_3Ph$_2$) and multiplets (δ 7.0–7.9 ppm, 2PCH$_3$*Ph*$_2$) in agreement with the η^2 coordination of the CO_2 ligand with palladium to make the $PMePh_2$ ligands nonequivalent. The $^{31}P\{^1H\}$ NMR spectrum (161.8 MHz at −35 °C, in CD_2Cl_2, referenced to external $P(OMe)_3$) also shows the two coordinated tertiary phosphine ligands as an AB quartet (δ_A 18.2 ppm, δ_B 14.9 ppm, J_{AB} = 42 Hz). In the $^{13}C\{^1H\}$ NMR spectrum (100.5 MHz at −35 °C, in CD_2Cl_2) of 3, a very weak signal arising from the CO_2 ligand is observed at δ 166.2 ppm in agreement with the reported value of δ 159.28 ppm for the η^2-coordinated CO_2 with nickel.[6] The $^{13}C\{^1H\}$ NMR of a $^{13}CO_2$-enriched sample (ca. 11%) shows a doublet of doublets pattern (Figure 1) with $J_{P\text{-}C\ trans}$ = 4.7 Hz and $J_{P\text{-}C\ cis}$ = 3.7 Hz in support of the structure with η^2-bonded CO_2 lying in the molecular plane.

Heating complex 3 in the solid state at 100 °C under argon or in vacuo caused rapid thermolysis (within 0.5 min) with liberation of 1.0 equiv of CO_2. On the other hand, the decomposition course is different in solution (Scheme 2). The two-doublets pattern arising from the nonequivalent $PMePh_2$ ligands in the ^1H NMR spectrum of 3 in CD_2Cl_2 at −30 °C is converted into a doublet arising

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

[1] Review: (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988,** *88,* 747. (b) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 661. (c) Aresta, M.; Forti, G. *Carbon Dioxide as a Source of Carbon. Biochemical and Chemical Uses*; D. Reidel: Dordrecht, The Netherlands, 1987. (d) Ito, T.; Yamamoto, A. In *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S. Yamazaki, N., Eds.; Kodansha: Tokyo, Japan, 1981. (e) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983,** 22, 129.

[2] For some examples of M–CO_2 complexes see: (a) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* **1975,** 636. (b) Alvarez, R.; Carmona, E.; Marín, J. M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986,** *108,* 2286. (c) Tanaka, H.; Nagao, H.; Peng, S. M.; Tanaka, K. *Organometallics* **1992,** *11,* 1450. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985,** *107,* 2985. (e) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983,** *105,* 5914. (f) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981,** 1145. (g) Gibson, D. H.; Ye, M.; Richardson, J. F. *J. Am. Chem. Soc.* **1992,** *114,* 9716. (h) See ref 8c. (i) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982,** *104,* 5082.

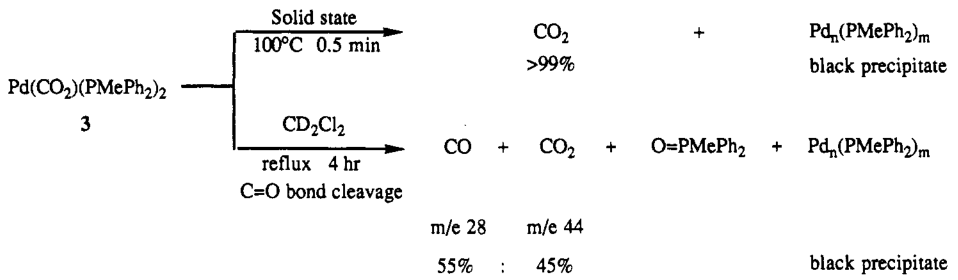
[3] (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Heidelberg, Germany, 1980. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.

[4] (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979,** *168,* 375. (b) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980,** *102,* 6457.

[5] Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977,** 708.

[6] Aresta, M.; Gobetto, R.; Quaranta, E.; Tommasi, I. *Inorg. Chem.* **1992,** *31,* 4286.

Scheme 2



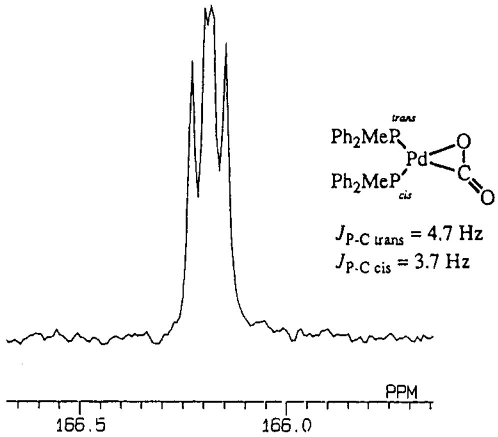


Figure 1. Part of the $^{13}C\{^1H\}$ NMR spectrum of Pd$(CO_2)(PMePh_2)_2$ (**3**) with $^{13}CO_2$ enrichment of 11%.

from O=PMePh$_2$ and a "filled-in" doublet pattern[7] after heating the solution at 40 °C for 1 h. The "filled-in" doublet pattern suggests the presence of an intermediate having the equivalent PMePh$_2$ ligands in mutually cis positions. On further heating the "filled-in" doublet pattern completely disappeared, leaving only the resonance of methyldiphenylphosphine oxide. On the other hand, in the $^{13}C\{^1H\}$ NMR of a similarly treated solution, decrease of the original doublet of doublets pattern, as shown in Figure 1, and appearance of a triplet (δ 167.4 ppm, J_{P-C} = 4 Hz) was observed. The triplet also disappeared after further heating. The "filled-in" doublet in the ^1H NMR and the triplet in the $^{13}C\{^1H\}$ NMR are ascribed to an intermediate formed in the process of thermolysis.[8] The GC–MS analysis of the gas phase of the reaction system indicated the formation of CO and CO$_2$ in a ratio of 55:45. The results show that the thermolysis in solution caused the cleavage of one of the two C=O bonds in the coordinated CO$_2$ ligands through an intermediate in which CO$_2$ is bound to palladium in such a manner as to make PMePh$_2$ ligands equivalent.[10]

Treatment of the CO$_2$-coordinated complex **3** with various electrophiles such as MeI, PhI, phenylacetylene, and Me$_3$OBF$_4$ led to decomposition of **3**. Treatment of **3** with 2 equiv of Me$_3$SiOSO$_2$CF$_3$ caused the formation of Me$_3$SiSiMe$_3$ and *cis*-Pd(OSO$_2$CF$_3$)$_2$(PMePh$_2$)$_2$,[11] whereas the reaction of Me$_3$SiCl with **3** gave Me$_3$SiSiMe$_3$ and a 1:1 *cis* and *trans* mixture of PdCl$_2$(PMePh$_2$)$_2$.[12]

The coordinated CO$_2$ in complex **3** can be partly converted into formic acid (3%/Pd)[13,14] on treatment of **3** with 2 equiv of PhSH at −20 °C with formation of *trans*-Pd(SPh)$_2$(PMePh$_2$)$_2$ (**4**), H$_2$, and CO$_2$. Neither free CO nor CO-coordinated species were observed in this reaction system.[15] Complex **4** can be independently prepared by treatment of **1** with PhSH (2 equiv) and by reaction of the methyl acrylate coordinated Pd(0) complex **2** with PhSSPh (Scheme 3).[16]

The formation of formic acid was also observed in the reaction of **3** with H$_2$ under CO$_2$ at room temperature in 12% yield. The formation of formic acid may proceed by insertion of CO$_2$ into palladium dihydride formed on reaction of H$_2$ with Pd(0) followed by reductive elimination of the hydrido and formate ligands. Aresta et al. reported the formation of a hydrido–formate complex on reaction of H$_2$ with Ni(CO$_2$)(PCy$_3$)$_2$.[6] The catalytic conversion of H$_2$ and CO$_2$ into formic acid (isolated as the ammonium salt) at room temperature was achieved by using PdCl$_2$L$_2$ (L = PMe$_3$, PMePh$_2$, PPh$_3$) as catalysts (Scheme 4). The formation of formic acid may take the course of the first hydrogenation of PdCl$_2$L$_2$ with H$_2$ to produce a palladium

---

[7] Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *50*, 14.

[8] The possibility that these resonances arise from the fluxional property of the CO$_2$-coordinated complex, as discussed in a recent report[6,9] dealing with the property of a CO$_2$-coordinated nickel complex, is excluded since no change is observed in the patterns of these resonances on cooling the solutions down to −30 to −80 °C.

[9] Jegat, C.; Fouassier, M.; Tranquille, M.; Mascetti, J.; Tommasi, I.; Aresta, M.; Ingold, F.; Dedieu, A. *Inorg. Chem.* **1993**, *32*, 1279.

[10] There are some reports on C=O cleavage of CO$_2$ by transition-metal complexes: (a) Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1991**, *10*, 3432. (b) Ito, T.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1975** 139. (c) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2213. (d) Bianchini, C.; Moli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698. (e) Folder, R. A.; Green, M. H.; Mackenzie, R. F.; Poland, J. S.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1973**, 426. (f) See Ref 2a. (g) Belmore, K. A.; Vanderpod, R. A.; Tsai, J.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004. (h) Tsai, J.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 29. (i) Aresta, M.; Nobile, C. F. *Inorg. Chim. Acta* **1977**, *24*, L49. (j) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033. (k) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767. (l) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (m) Fu, P.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 382. (n) Reinking, M. K.; Ni, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 6459. (o) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. (p) Alt, H. G.; Schwind, K. *J. Organomet. Chem.* **1987**, *321*, C9. (q) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *6*, 1805. (r) Tsuda, T.; Sanada, S.; Saegusa, T. *J. Organomet. Chem.* **1976**, *116*, C10.

[11] We have also observed other unidentified silyl compounds. ^1H NMR (CD$_2$Cl$_2$): δ 0.02 (s), 0.09 (s), 0.12 (s), 0.20 ppm (s).

[12] This reaction may be similar to the reaction Pd(PPh$_3$)$_4$ + Me$_3$SiCl → PdCl$_2$(PPh$_3$)$_2$ + Me$_3$SiSiMe$_3$: Stille, J. K.; Lau, K. S. *J. Am. Chem. Soc.* **1976**, *98*, 5841.

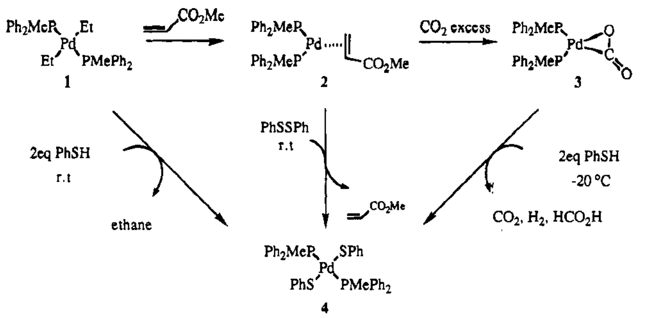
[13] Determined by GC–MS spectroscopy.

[14] Conversion of CO$_2$ into formic acid by use of transition-metal catalysts has been reported. For example: (a) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 863. (b) Khan, M. M. T.; Alligudi, S. B.; Shuka, S. J. *J. Mol. Catal.* **1989**, *51*, 47. (c) Tsai, J.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (d) Burgemeister, T.; Kastner, F.; Leitner, W. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 739.

[15] Reaction of Ni(CO$_2$)(PCy$_3$)$_2$ with PhSH has been reported: Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 450.

[16] Complex **4** was characterized by means of ^1H NMR, $^{31}P\{^1H\}$ NMR, and elemental analysis. ^1H NMR data (90 MHz, at room temperature, in CD$_2$Cl$_2$) of Pd–PCH_3Ph$_2$: δ 1.89 ppm, triplet, 2 × 3H. $^{31}P\{^1H\}$ NMR data (161.8 MHz, at room temperature, in CD$_2$Cl$_2$, referenced to external P(OMe)$_3$): δ 8.8 ppm, singlet. Anal. Calcd for the complex prepared by the reaction of **3** with PhSSPh, C$_{38}$H$_{36}$P$_2$S$_2$Pd: C, 63.2; H, 5.2. Found: C, 62.9; H, 5.0. Mp: 153–154 °C dec.

Scheme 3



Scheme 4

$$\underset{50\ \text{atm}}{CO_2} + \underset{50\ \text{atm}}{H_2} \xrightarrow[\text{2) } NH_3/H_2O]{\text{1) } PdCl_2L_2\ \text{benzene}/Et_3N/H_2O\ \text{r.t.}} HCO_2NH_4$$

L=PMe$_3$: 147%/Pd
=PMePh$_2$: 620%/Pd
=PPh$_3$: 1538%/Pd

hydride into which CO_2 may be inserted to produce a palladium formate. Further hydrogenation of the formate or reductive elimination will produce formic acid. In fact, NMR examination of a CD_2Cl_2 solution containing PdH(Cl)(PMe$_3$)$_2$[4a] and CO_2 at -40 °C indicated the formation of a formato complex (triplet at δ 9.7 ppm with J_{P-H} = 2 Hz).[17]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 05225229) from the Ministry of Education, Science and Culture and The Japan Securities Scholarship Foundation. We also wish to express our gratitude to Nippon Zeon Co., Ltd., for funding.

OM930655R

---

(17) For some examples of CO_2 insertion into a metal–hydrido bond, see: (a) Darensbourg, D. J.; Darensbourg, M. Y.; Goh, L. Y.; Ludvig, M.; Wiegreffe, P. *J. Am. Chem. Soc.* **1987**, *109*, 7539. (b) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. (c) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58. (d) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 371. (e) Misono, A.; Uchida, Y.; Hidai, M.; Kuse, T. *Chem. Commun.* **1968**, 981. (f) See ref 12c,d. (g) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. (h) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 297. (i) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.* **1990**, *112*, 9252. (j) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223. (k) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500. (l) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876.