CHEMISTRY LETTERS, pp. 851-854, 1976. Published by the Chemical Society of Japan

THE REACTIONS OF CARBON DIOXIDE WITH DIALKYL COMPLEXES OF PALLADIUM(II)

Takashi ITO, Hirotaka TSUCHIYA, and Akio YAMAMOTO
Research Laboratory of Resources Utilization, Tokyo Institute of
Technology, Ookayama, Meguro-ku, Tokyo 152

Dialkylpalladium complexes, $[Pd(CH_3)_2L_2]$ and $[Pd(C_2H_5)_2L_2]$, reacted with CO_2 to yield CO_2-coordinated complexes, $[Pd(CH_3)(CO_2)L_2]$ (L = PEt_3, **1**, and $PMePh_2$, **2** (isolated as an acetone solvate)) and $[Pd(C_2H_4)(CO_2)L_2]$ (L = PEt_3, **3**, and $PMePh_2$, **4**), respectively. Complexes **1** - **4** were isolated and characterized on the basis of elemental analysis, chemical reactions, IR, and ^1H-NMR spectral evidence.

In recent years much attention has been focused on the interaction of carbon dioxide with transition metal compounds.[1] In spite of a considerable number of hitherto known CO_2-coordinated and/or -inserted transition metal complexes, none has been reported on the palladium complex, although the catalytic ability of $[Pd(CO_3)(PPh_3)_2]$[2] and $[Pd(dpe)_2]$[3,4] (dpe = $Ph_2PCH_2CH_2PPh_2$) has been claimed in the catalytic fixation of CO_2 to produce formamides,[2] formates,[3] and formic acid.[4] Here we report the synthesis and characterization of several new CO_2-coordinated palladium complexes which were prepared by the reactions of gaseous carbon dioxide with some dialkyl complexes of palladium(II).[5]

On passing CO_2 through a colorless clear solution of trans-$[Pd(CH_3)_2(PEt_3)_2]$[6] in hexane at room temperature for ca. 15 h, the white precipitate gradually accumulated in the solution with an accompanying evolution of methane. Recrystallization of the precipitate from acetone yielded white crystals whose stoichiometry corresponded to $[Pd(CH_3)(CO_2)(PEt_3)_2]$ **1** on the basis of spectral and chemical evidence (vide infra). Similar reaction of cis-$[Pd(CH_3)_2(PMePh_2)_2]$[5] with CO_2 in toluene afforded $[Pd(CH_3)(CO_2)(PMePh_2)_2]$, recrystallization of which from acetone yielded white crystals **2** which contained one mole of acetone as a crystallization solvent.

$$[Pd(CH_3)_2L_2] + CO_2 \longrightarrow [Pd(CH_3)(CO_2)L_2] + CH_4$$

$$L = \begin{cases} PEt_3,\ \mathbf{1} \\ PMePh_2,\ \mathbf{2}\ \text{(as acetone solvate).} \end{cases}$$

Complexes **1** and **2** are insensitive to air in a solid state at room temperature and decomposed at 85-90°C and 106-110°C, respectively in vacuo.

Treatment of **1** and **2** with conc. H_2SO_4 released quantitative amounts of methane and CO_2 on the basis of their formula. Decomposition of **1** with D_2SO_4 evolved a theoretical amount of CH_3D. Thermolysis of **2** in vacuo at 220°C released CH_4, C_2H_6 and CO_2. Reaction of **1** and **2** with methyl iodide led to the formation of $[Pd(CH_3)IL_2]$

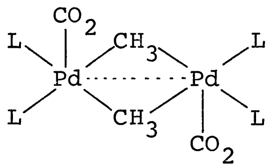
Table 1. IR spectra of Pd-CO_2 complexes (KBr, cm^{-1})

Compounds	CO_2 bands	δ(C-H)
$[Pd(CH_3)(CO_2)(PEt_3)_2]$ **1**	2610w, 1610s, 1350s, 825m	1180m[a)]
$[Pd(CH_3)(CO_2)(PMePh_2)_2]\cdot(CH_3)_2CO$ **2**	2605w, 1605s, 1405s, 1350s, 835m	1185m[a)]
$[Pd(C_2H_4)(CO_2)(PEt_3)_2]$ **3**	2600w, 1630s, 1350s, 830m	1160m[b)]
$[Pd(C_2H_4)(CO_2)(PMePh_2)_2]$ **4**	2600w, 1605s, 1400s, 1360s, 832m	1170m[b)]

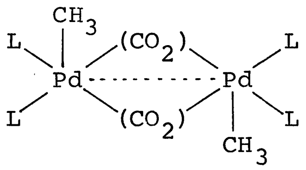
a) δ(C-H) of Pd-CH_3. b) δ(C-H) of coordinated C_2H_4.

with the accompanying evolution of CH_4 and CO_2. All the chemical evidence suggests the presence of CO_2 and CH_3 moieties coordinated to Pd in complexes **1** and **2**. The IR absorptions assignable to the coordinated CO_2 in **1** and **2** are listed in Table 1. The similar absorptions have been reported for $[Rh_2(CO_2)_2(CO)_2(PPh_3)_3]\cdot C_6H_6$[8)] and $[Cu(O_2CCH_3)(CO_2)L_2]$ (L = PPh_3[9)] and $P(C_6H_{11})_3$[10)]). δ(C-H) Values (also included in Table 1) and ν(Pd-C) (530 cm^{-1} for **1** and not discernible for **2**) are all somewhat higher than those of the corresponding parent dialkyl complexes.[5)] The ^{1}H-NMR spectra (100 MHz at 25°C, chemical shifts are in δ values with respect to tetramethylsilane as an external standard, downfield positive) of **1** in $(CD_3)_2CO$ and **2** in CD_2Cl_2 were consistent with the postulated formula. **1**: 0.03 ppm (triplet, $^3J_{P-H}$ = 6 Hz, 3H, Pd-C$\underline{H}_3$), 1.75 ppm (multiplet, 12H, P-C$\underline{H}_2$-), and 1.20 ppm (quintet, $^3J_{P-H} \approx {}^3J_{H-H} \approx$ 8 Hz, 18H, P-C-C$\underline{H}_3$); **2**: -0.03 ppm (broad singlet, 3H, Pd-C$\underline{H}_3$), 1.86 ppm (singlet, 6H, P-C$\underline{H}_3$), 7.56 and 7.36 ppm (multiplet, 20H, P-$\underline{Ph}$), and 2.07 ppm (singlet, ~6H, $(C\underline{H}_3)_2CO$). The broad singlet at -0.03 ppm in **2** split into a triplet by lowering the temperature to -40°C indicating the presence of a dissociation of **2** in the solution at 25°C.

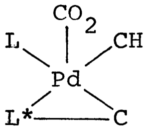
The fact that complexes **1** and **2** give well-resolved ^{1}H-NMR signals with Pd-CH_3 resonances at the normal positions indicates that the complex is diamagnetic and the central palladium metal should be divalent. In order to meet these requirements, the binuclear structure with a spin-spin interaction between two Pd atoms of the types either [I] or [II] are postulated as possible structures for **1** and **2**. The molecular weight measurement (vapor pressure osmometry in benzene) for **1** and **2** exhibited the values close to the mononuclear structure (460 for **1** and 550 for **2**). However, these findings do not exclude the possibility of [I] or [II], since the



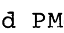
[I]



[II]



[III]

L*-C = $PEt_2(CH_2CH_2)$ for **1** and PMe(Ph)() for **2**.

possible dissociation of the tertiary phosphine ligand in **1** and **2** in the solution, as suggested by the NMR spectral observation, may cause the decrease in the apparent molecular weight value. The alternative possible structure [III], in which metallation of carbon atoms in the phosphorus ligand is involved, can not be ruled out at the present time, as the metallation of phenyl _ortho_ carbon in the arylphosphine complexes is now amply demonstrated. A few examples of metallation of alkyl carbon in some tertiary phosphine complexes is also known for _e.g._, $[\mathrm{Ru(Me_2PCH_2CH_2PMe_2)_2}]$,12) $[\mathrm{PtCl(\text{-}CH_2CH_2CH_2PBu^t{}_2)(PBu^t{}_2Pr^n)}]$,13) and $[\overline{\mathrm{PdCl\{P(\underline{o}\text{-}tolyl)_2(C_6H_4CH_2}})\}\{\mathrm{P(\underline{o}\text{-}tolyl)_3}\}]$.14)

Bubbling CO_2 into a hexane solution of the diethyl complex, _trans_-$[\mathrm{Pd(C_2H_5)_2(PEt_3)_2}]$,5) at -20 to -40°C for 15 h yielded a thermally unstable white powder which was characterized as a zerovalent palladium complex, $[\mathrm{Pd(C_2H_4)(CO_2)(PEt_3)_2}]$ **3** (_vide infra_). Similarly obtained was $[\mathrm{Pd(C_2H_4)(CO_2)(PMePh_2)_2}]$ **4** by the reaction of $[\mathrm{Pd(C_2H_5)_2(PMePh_2)_2}]$5) with CO_2 in toluene at -20 to -40°C for 15 h. Complexes **3** and **4** decomposed at room temperature and 50°C, respectively, releasing CO_2 and ethylene

$$[\mathrm{Pd(C_2H_5)_2L_2}] + \mathrm{CO_2} \longrightarrow [\mathrm{Pd(C_2H_4)(CO_2)L_2}] + \mathrm{C_2H_6}$$

$$L = \begin{cases} \mathrm{PEt_3}, & \mathbf{3} \\ \mathrm{PMePh_2}, & \mathbf{4} \end{cases}$$

(1:1) whose amounts were close to the theoretical values calculated on the basis of their formula. Treatment of **1** and **2** with H_2SO_4 evolved CO_2 and ethane (1:1). Their reaction with an excess amount of methyl iodide yielded $[\mathrm{PdI_2L_2}]$ (L = PEt_3 and $PMePh_2$) with an accompanying evolution of CO_2, C_2H_4, CH_4, and C_2H_6. The IR spectra of **3** and **4** are very similar to those of **1** and **2**, respectively. Characteristic IR absorptions of **3** and **4** are included in Table 1. A similar value of 1203 cm^{-1} for δ(C-H) of the coordinated ethylene has been reported for $[\mathrm{Pd(C_2H_4)(PPh_3)_2}]$.15) The ^{1}H-NMR spectrum of **3** (in $(CD_3)_2CO$) and **4** (in CD_2Cl_2) at -40°C showed only signals due to the tertiary phosphine ligand. **3**: 1.72 ppm (multiplet, 2H, P-C$\underline{H}_2$-) and 1.14 ppm (quintet, $^3J_{P-H} \approx {}^3J_{H-H} \approx 8$ Hz, 3H, P-C-C$\underline{H}_3$); **4**: 1.82 ppm (broad singlet, 6H, P-C$\underline{H}_3$) and 7.63 and 7.42 ppm (multiplet, 20H, P-$\underline{Ph}$). Although the signal due to the coordinated ethylene could not be observed in the spectra measured at -40°C, the spectrum of **4** at 25°C exhibited a new signal at 3.35 ppm. The absence of a signal due to the coordinated ethylene at -40°C may be attributable to the partial dissociation of the ethylene ligand, _i.e._, the slow exchange between coordinated and uncoordinated ethylene molecules might have caused the apparent disappearance of their signals.

Isolation of Pd(0) complexes coordinated with both CO_2 and ethylene may have implications related to the reported CO_2 effect on the catalytic activity and selectivity in the dimerization of butadiene catalyzed by Pd(0) complexes, such as $[\mathrm{Pd(PPh_3)_4}]$,16,17) $[\mathrm{Pd(PEt_3)_3}]$, $[\mathrm{Pd\{P(C_6H_{11})_3\}_2}]$, and $[\mathrm{Pd(PPh_3)_3}]$,18) where direct interaction of CO_2 with a palladium complex has been postulated in the catalytic reaction.18)

Complexes **1** - **4** represent the first examples of the CO_2-coordinated palladium complex, although the formation of the carbonate complex $[\mathrm{Pd(CO_3)(PPh_3)_2}]$ has been reported in the reaction of Pd(0) complex with both O_2 and CO_2.19)

Support of this work by the Kawakami Foundation is gratefully acknowledged.

References

1) See for example, M. E. Vol'pin and I. S. Kolomnikov, Pure Appl. Chem., 33, 567 (1973); T. Ito and A. Yamamoto, Yuki Gosei Kagaku Kyokai Shi, 34, 308 (1976).
2) P. Haynes, L. H. Slaugh and J. F. Kohnle, Tetrahedron Lett., 1970, 365.
3) Y. Inoue, Y. Sasaki, and H. Hashimoto, J. Chem. Soc., Chem. Commun., 1975, 718.
4) H. Izumida, Y. Sasaki, Y. Inoue, and H. Hashimoto, Abstr. No. 848, 34th National Meeting of the Chemical Society of Japan, Hiratsuka, April 1976.
5) Recently we succeeded in the isolation of serieses of dialkyl complexes of palladium, $[PdR_2L_2]$ (R = CH_3, C_2H_5, and n-C_3H_7; L = PEt_3, $PMePh_2$, and $\frac{1}{2}(Ph_2PCH_2CH_2PPh_2)$) from the systems consisted of $[Pd(acac)_2]$ (acac = acetylacetonato), L and $AlR_2(OC_2H_5)$; H, Tsuchiya, T. Ito, and A. Yamamoto, Abstr. No. 875, 34th National Meeting of the Chemical Society of Japan, Hiratsuka, April 1976. The detailed report will be published elsewhere.
6) The cis-isomer of this compound has been prepared by Calvin and Coates by the reaction of CH_3Li with trans-$[PdCl_2(PEt_3)_2]$ (see Ref. 7). The trans-configuration of the complex prepared in the present study was confirmed by ^1H-NMR spectroscopy.
7) G. Calvin and G. E. Coates, J. Chem. Soc., 1960, 2008.
8) I. S. Kolomnikov, T. S. Belopotapova, T. V. Lysyak, and M. E. Vol'pin, J. Organomet. Chem., 67, C25 (1974).
9) A. Miyashita and A. Yamamoto, J. Organomet. Chem., 49, C57 (1973); a full paper, by Miyashita and Yamamoto, J. Organometal. Chem., in press.
10) T. Ikariya and A. Yamamoto, J. Organomet. Chem., 72, 145 (1974).
11) E.g., G. W. Parshall, Acc. Chem. Res., 3, 139 (1970).
12) F. A. Cotton, B. A. Franz, and D. L. Hunter, Chem. Commun., 1974, 765.
13) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, Chem. Commun., 1970, 1176.
14) D. M. Fenton, J. Org. Chem., 38, 3192 (1973).
15) P. Fitton, M. P. Johnson, and J. E. Mckeon, Chem. Commun., 1968, 6.
16) J. F. Kohnle, L. H. Slaugh, and K. L. Nakamaye, J. Am. Chem. Soc., 91, 5904 (1969).
17) K. E. Atkins, W. E. Walker, and R. M. Manyik, Chem. Commun., 1971, 330.
18) A. Musco and A. Silvani, J. Organomet. Chem., 88, C41 (1975).
19) C. J. Nyman, C. E. Wymore, and G. Wilkinson, J. Chem. Soc., A, 1968, 561.

(Received July 6, 1976)