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REACTIONS OF CARBON DIOXIDE WITH PALLADIUM COMPLEXES. SYNTHESIS AND CHARACTERIZATION OF CARBAMATO COMPLEXES OF PALLADIUM(II)[1]

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A variety of new carbamatopalladium complexes, $[PdMe(O_2CNRR')L_2]$ (L = tertiary phosphine; R,R' = H, alkyl, and phenyl), were prepared by direct reactions of dimethylpalladium complexes, $[PdMe_2L_2]$, with carbon dioxide in the presence of amines. These complexes were characterized by means of elemental analysis, IR and ^{1}H-NMR spectroscopy and chemical reactions. A new μ-carbonatopalladium complex, $[Pd_2Me_2(\mu\text{-}CO_3)(PPh_3)_3]$, was prepared by heating the toluene solution of $[PdMe(O_2CNH_2)(PPh_3)_2]$.

Although the catalytic activities of palladium compounds have been reported in the syntheses of formamides,[2] formates,[3] formic acid,[4] and lactone[5] starting from carbon dioxide, only a few attempts have been made on the isolation of complexes from reaction systems consisted of palladium compounds and carbon dioxide.[1,6,7] Previously we reported that dialkylpalladium complexes, $[PdR_2L_2]$ (R = Me, Et; L = PEt_3, $PMePh_2$), reacted with gaseous carbon dioxide at normal pressure to give CO_2-coordinated complexes.[1] Subsequent X-ray crystallographic study revealed that the complexes thus obtained were in fact hydrogencarbonato complexes, $[PdR(OCOOH)L_2]_2$, which are thought to be produced by the intervention of water, a possible contaminant in the carbon dioxide gas (eq.1).[6]

$$2[PdR_2L_2] + 2H_2O + 2CO_2 \longrightarrow [PdR(OCOOH)L_2]_2 + 2CH_4 \qquad (1)$$
$$R = Me, Et;\ L = PEt_3,\ PMePh_2$$

Now we report that a series of carbamatopalladium complexes can be prepared by the reaction related to (1) between dimethylpalladium complexes and dry carbon dioxide in the presence of primary and secondary amines. Although the syntheses of carbamato transition metal complexes have been reported for Ti, Zr, Nb, Ta, W[8], Mo[9], Cu[10], and Ru[11] either from amido,[8,9] alkoxo,[10] or hydrido complexes,[11] there is no precedent of the unambiguous isolation of a carbamatopalladium complex.

The reactions of $[PdMe_2L_2]$ (L = PEt_3,[12] $PMePh_2$,[12] PPh_3[13]) with alkyl (or aryl) amines in a molar ratio 1 : 2-3 in THF or Et_2O in an atmosphere of carbon dioxide at room temperature afforded trans-alkyl(or aryl)carbamatomethylbis(tertiary phosphine)palladium(II) complexes, $[PdMe(O_2CNRR')L_2]$ (**1**-**3**), with accompanying evolution of one mol of methane per palladium (eq. 2).

$$[\mathrm{PdMe_2L_2}] + \mathrm{HNRR'} + \mathrm{CO_2} \xrightarrow{\text{THF or Et}_2\text{O}} \underset{\mathbf{1}\ -\ \mathbf{3}}{[\mathrm{PdMe(O_2CNRR')L_2}]} + \mathrm{CH_4} \qquad (2)$$

L	PEt_3	$PMePh_2$	PPh_3				
R	H	H	Et	H	H	H	H
R'	Ph	Ph	Et	n-Bu	CH_2Ph	H	Ph
	1	**2**	**3a**	**3b**	**3c**	**3d**	**3e**

Since dimethylpalladium complexes did not react with amines in the absence of carbon dioxide[14)] but reacted with carboxylic acids such as acetic acid readily forming carboxylatomethylbis(tertiary phosphine)palladium(II) with evolution of methane,[15)] it is conceivable that the reactions (2) may proceed via a process as shown in eq. 3. Thus amines react with carbon dioxide prior to the reaction with the complex to form carbamic acids,[16)] which then attack the dimethyl complex to yield carbamato complexes **1** - **3**.

$$\begin{aligned} &\mathrm{HNRR'} + \mathrm{CO_2} \rightleftharpoons \mathrm{HO_2CNRR'} \\ &[\mathrm{PdMe_2L_2}] + \mathrm{HO_2CNRR'} \longrightarrow [\mathrm{PdMe(O_2CNRR')L_2}] + \mathrm{CH_4} \end{aligned} \qquad (3)$$

A similar reaction path has been proposed for the formation of carbamato complexes of W, Ti, Zr, Nb, and Ta.[8)]

Among amines tested, only diphenyl amine did not afford carbamato complexes on the reaction with dimethylpalladium complex even in the presence of CO_2, but gave amido complex **4** (eq. 4).

$$\underset{\mathrm{L}\,=\,\mathrm{PEt_3,\ PMePh_2}}{[\mathrm{PdMe_2L_2}] + \mathrm{HNPh_2}} \xrightarrow{\mathrm{CO_2}} \underset{\mathbf{4}}{[\mathrm{PdMe(NPh_2)L_2}]} + \mathrm{CH_4} \qquad (4)$$

Complex **4** is thought to be formed via a decarboxylation from the carbamatopalladium intermediate which may be too unstable to be isolated.

The carbamatopalladium complexes thus obtained are recrystallizable from hot toluene as white crystals except for **2**, **3d** and **3e** which tend to decompose in solution. Satisfactory elemental analyses (C, H, and N) have been obtained for all complexes isolated. They are diamagnetic and relatively insensitive to air. Treatment of complexes **1** - **3** with concentrated H_2SO_4 liberated 1 mol of methane and 1 mol of carbon dioxide per palladium.

The characteristic IR bands (KBr disc) due to carbamato ligands of **1** - **3** are observed in the range of 3170 - 3455 (ν(N-H)) and 1635 - 1263 cm^{-1}, and in the neighborhood of 800 cm^{-1}. The characteristic bands of **3a** in the 1600 - 1200 cm^{-1} region (1550, 1480, 1409, and 1298 cm^{-1}) were found to be similar to those of the reported carbamatoruthenium complexes, $[RuH(O_2CNMe_2)(PPh_3)_3]$ and $[Ru(O_2CNMe_2)(PMe_2Ph)_4]PF_6$ (1538, 1502, 1403, and 1272 cm^{-1}, and 1565, 1465, 1412, and 1270 cm^{-1}, respectively).[11)] The spectroscopic evidence suggests that the carbamato ligand in **3a** is coordinated to palladium in a bidentate way via two oxygen atoms, since the bidentate coordination of carbamato ligand in $[Ru(O_2CNMe_2)(PMe_2Ph)_4]PF_6$ has been established by its X-ray crystallographic study.[11)]

In ^{1}H-NMR spectra of complexes **1** - **3**, signals due to Pd-Me are observed at

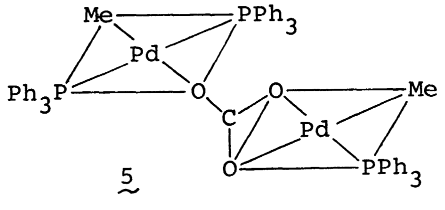
Table. Reactions of $[PdMe(O_2CNRR')(PPh_3)_2]$ with MeI

-NRR'		Products (mol/mol complex)		
		RR'NCOOMe	CO_2	MeOCOOMe
$-NEt_2$	**3a**	0.76	0.25	—
$-NHBu^n$	**3b**	0.80	0.11	—
$-NHCH_2Ph$	**3c**	1.00	0.11	—
$-NH_2$	**3d**	0.52	0.20	0.05
-NHPh	**3e**	0	0.24	0.01

-0.22 to -0.02 ppm (100 MHz, in $CDCl_3$, chemical shifts are in δ values with respect to tetramethylsilane as an external standard, downfield positive) as a triplet at room temperature (**1** and **2**) or at -40°C (**3a**-**3d**). (**1**, -0.02 ppm, $^3J_{P-H}$ = 4 Hz; **2**, -0.11 ppm, $^3J_{P-H}$ = 4.6 Hz; **3a**, -0.22 ppm; **3b**, -0.22 ppm; **3c**, -0.16 ppm; **3d**, -0.11 ppm. Pd-<u>Me</u> signals in **3a** - **3d** are broad triplets making the estimation of their coupling constants obscure.) Furthermore, methyl signals of PEt_3 in **1** and of $PMePh_2$ in **2** were found as a quintet and a triplet, respectively. (**1**, 1.07 ppm, quintet, J_{P-H} = 8 Hz, $P-C-C\underline{H}_3$; **2**, 1.91 ppm, triplet, J_{P-H} = 1.10 Hz, $P-C\underline{H}_3$). These coupling patterns of Pd-<u>Me</u> and methyl groups of phosphine ligands are consistent with the trans configuration of the square planar complexes.

The results of the reactions of the present carbamato complexes with MeI at room temperature are listed in the Table. Complexes **3a**, **3b**, and **3c**, on the reaction with MeI, formed corresponding carbamic acid methyl esters in high yields and some carbon dioxide accompanied by small amounts of methane and ethane. Presence of $[PdI_2(PPh_3)_2]$ and $[PdMe(I)(PPh_3)_2]$ in the reaction residue was confirmed by IR spectroscopy. On the other hand, the reaction of **3d** and **3e** with MeI gave dimethyl carbonate (<u>vide infra</u>) in addition to carbon dioxide and corresponding carbamic acid methyl ester.

When $[PdMe(O_2CNH_2)(PPh_3)_2]$ (**3d**) was heated in toluene at 80° for 2h, an unexpected complex, $[Pd_2Me_2(\mu-CO_3)(PPh_3)_3]$ (**5**), was formed. Complex **5** was characterized by means of elemental analysis (C, H, and N), IR, ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy[17] and some chemical reactions. From the spectroscopic evidence of **5**, it is suggested that **5** has the structure as shown below, which is very similar to that of the reported $[Rh_2(\mu-CO_3)(PPh_3)_5]$.[18] The molecular structure of the latter has been established by X-ray crystallographic study. This is the first example, to our knowledge, of the synthesis of μ-carbonato complex from carbamato complex. Recently, the syntheses of similar type complexes with μ-carbonato ligands have been reported for Rh[19] and Cu[20], and Mo[21] by the processes involving corresponding hydrogencarbonato complexes and CO_2-coordinated complex, respectively.



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Acidolysis of **5** with H_2SO_4 released one mol of methane and half mol of CO_2 per palladium. The reaction of **5** with MeI afforded 0.54 mol of dimethyl carbonate and 0.42 mol of carbon dioxide on the basis of its formula. Formation of dimethyl carbonate in the reaction of $[PdMe(O_2CNH_2)(PPh_3)_2]$ (**3d**) with MeI

(Table) can be explained by considering the formation of an intermediate complex **5** which affords dimethyl carbonate on treatment with MeI on the reaction with MeI. The fate of the amino moiety in **3d** is presently under investigation.

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