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Synthesis, characterization, and carbonylation reactions of methylpalladium amide, carbamate, and alkyl carbonate complexes *

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Abstract

A series of *trans*- and *cis*-methylpalladium carbamate complexes $PdMe(OCONRR')L_2$ (L = tertiary phosphine; R, R' = H, alkyl, and phenyl) was prepared by the reaction of dimethylpalladium complexes with primary or secondary amine and carbon dioxide. When diphenylamine was used, methylpalladium amide complexes *trans*-$PdMe(NPh_2)L_2$ (L = PMe_3 and PEt_2Ph) were isolated instead of carbamates. The carbamate and amide complexes thus prepared were characterized by IR and NMR spectroscopy and elemental analysis. The carbamate complex *trans*-$PdMe(OCONEt_2)(PMe_3)_2$ released one of the PMe_3 ligands on recrystallization to form a dimeric compound $Pd_2Me_2(\mu\text{-}OCONEt_2)_2(PMe_3)_2$, whose structure was determined by X-ray diffraction study. The carbamate complexes reacted with carbon monoxide under pressure to give corresponding α-keto amide ($MeCOCONRR'$) and amide ($MeCONRR'$). Reactions of dimethylpalladium complexes with alcohols and carbon dioxide gave methylpalladium alkyl carbonate complexes *trans*-$PdMe(OCOOR)L_2$ (R = Me, ^tBu; L = PMe_3, PPh_3). Treatment of alkyl carbonate complexes with carbon monoxide afforded the corresponding alkyl acetate as the sole carbonylation product.

1. Introduction

Although amide complexes for the early transition metals in high oxidation states are common, their analogues for the late transition metals have been less thoroughly explored and they have only recently begun to attract attention [1,2]. The most common method for the synthesis is metathetical replacement of an anionic ligand by amide anion or deprotonation of a complexed amine.

In the course of our study exploring the utility of carbon dioxide in organic synthesis with organotransition metal complexes, we found that dimethylpalladium complexes bearing tertiary phosphine ligands react with diphenylamine under an atmosphere of carbon dioxide to give methylpalladium amide complexes (eqn. (1)) [3]. In contrast to diphenylamine, the more basic aliphatic amines and aniline gave methylpalladium carbamate complexes on reaction with dimethylpalladium and carbon dioxide (eqn. (2)). Since dimethylpalladium complexes are inert towards amines including diphenylamine in the absence of carbon dioxide, it was assumed that the diphenylamide complexes were formed by decarboxylation of diphenylcarbamate intermediates generated from dimethyl complexes and diphenylcarbamic acid (Scheme 1). The other, more basic amines form more stable carbamate ligands and did not give amides by decarboxylation.

$$PdMe_2L_2 + HNPh_2 \xrightarrow[Et_2O,\ \text{room temp.}]{+CO_2} PdMe(NPh_2)L_2 + CH_4 \quad (1)$$

[L = PEt_3 and $PMePh_2$]

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$$PdMe_2L_2 + HNRR' \xrightarrow[Et_2O,\ room\ temp.]{+CO_2} PdMe(OCONRR')L_2 + CH_4 \quad (2)$$

$$\left[\begin{array}{l} L = PPh_3,\ HNRR' = HNEt_2,\ BuNH_2, \\ \quad PhCH_2NH_2,\ NH_3,\ H_2NPh \\ L = PEt_3 \text{ and } PMePh_2,\ HNRR' = H_2NPh \end{array}\right]$$

The reactivities of the carbamate ligands may be altered on further reaction of the carbamate complexes with other reagents so that the decarboxylation may be promoted to release the reactive amide entities. In this paper we describe further attempts to prepare methylpalladium amide and carbamate complexes using a variety of dimethylpalladium complexes having mono-

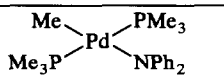
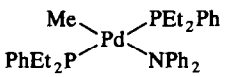
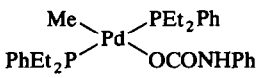
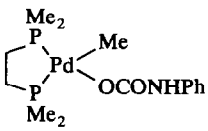
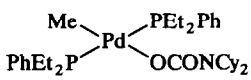
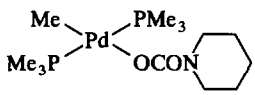
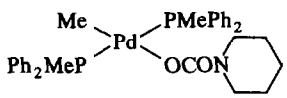
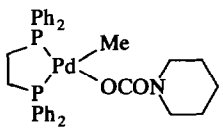
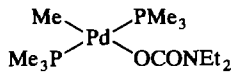
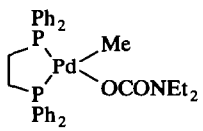
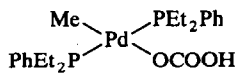
$$HNPh_2 + CO_2 \rightleftharpoons Ph_2NCOOH$$

$$PdMe_2L_2 + Ph_2NCOOH \longrightarrow PdMe(OCONPh_2)L_2 + CH_4$$

$$PdMe(OCONPh_2)L_2 \longrightarrow PdMe(NPh_2)L_2 + CO_2$$

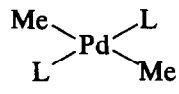
Scheme 1. Proposed mechanism for formation of methylpalladium amide complex.

TABLE 1. Methylpalladium carbamate and amide complexes

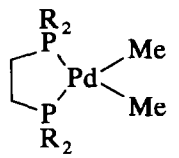
Starting complex	Amine	Product		Anal. Found (Calcd.) (%)		
				C	H	N
1	$HNPh_2$		(6)	51.2 (51.7)	7.1 (7.1)	3.1 (3.2)
2	$NHPh_2$		(7)	63.8 (63.7)	7.4 (6.9)	2.2 (2.3)
2	H_2NPh		(8)	56.9 (57.0)	6.7 (6.7)	2.5 (3.4)
4	H_2NPh		(9)	40.8 (41.0)	7.0 (6.6)	3.4 (3.4)
2	$HNCy_2$ [a]		(10)	59.6 (60.2)	8.4 (8.1)	1.8 (2.1)
1	piperidine		(11)	38.7 (38.9)	8.0 (7.8)	3.5 (3.5)
3	piperidine		(12)	61.2 (61.0)	6.6 (6.0)	2.1 (2.2)
5	piperidine		(13)	60.8 (61.2)	5.7 (5.8)	2.0 (2.2)
1	$HNEt_2$		(14)	37.2 (37.0)	8.6 (8.0)	3.5 (3.6)
5	$HNEt_2$		(15)	59.9 (60.4)	5.5 (5.9)	1.9 (2.2)
2	HNMePh [b]		(16) [c]	50.7 (50.4)	6.6 (6.5)	0.0 (0.0)

[a] Cy = cyclohexyl. [b] See text. [c] The compound has a dimeric structure (see text).

dentate and bidentate phosphine ligands (Chart 1). Reactivities of the methylpalladium amide and carbamate complexes prepared are then examined with particular attention to the reactions with carbon monoxide in the light of our interest in the palladium-catalyzed double carbonylation of organic halides to give α-keto amides [4].



L = PMe_3 (1); PEt_2Ph (2); $PMePh_2$ (3)



R = Me (4); Ph (5)

Chart 1. Dimethylpalladium complexes used in this study.

2. Results and discussion

2.1. Preparation of methylpalladium carbamate and amide complexes

Dimethylpalladium complexes (1–5, Chart 1) were treated with primary and secondary amines (2–3 equiv) in Et_2O at room temperature under an atmosphere of carbon dioxide. The reaction gave the methylpalladium amide and carbamate complexes listed in Table 1. Of the amines tested, only diphenylamine gave amide complexes (6 and 7). The reaction with diphenylamine proceeded smoothly with *trans*-dimethylpalladium complexes bearing monodentate phosphine ligands. On the other hand, in the reactions of *cis*-dimethyl complexes (4 and 5) with diphenylamine, the starting palladium compounds were recovered unreacted. When compound 2 was treated with *N*-methylaniline in the presence of carbon dioxide, the hydrogen carbonate complex $[PdMe(OCOOH)(PEt_2Ph)_2]_2$ (16) was isolated in place of carbamate and amide complexes. The formation of complex 16 is probably due to the hydrolysis of the intermediate carbamate complex by residual moisture in the system. In fact, treatment of 2 with *N*-methylaniline with moist carbon dioxide gave the same complex. Formation of such hydrogen carbonate complexes has been observed in several studies [5–7].

The amide complexes (6 and 7) were obtained as yellow solids and the carbamate and hydrogen carbonate complexes (8–15 and 16, respectively) were isolated as white crystalline solids. All the compounds were characterized by elemental analysis (Table 1) and IR and NMR spectroscopy (Table 2); $^{13}C\{^1H\}$ NMR data

TABLE 2. IR and NMR data of methylpalladium carbamate and amide complexes

Complex	IR data (cm^{-1}) [a]		^1H NMR (δ) [b]			$^{31}P\{^1H\}$ NMR (δ) [c]
	ν(CO)	ν(NH)	PdMe	PMe or PEt	amino group	
6	–	–	−0.28 (t, J = 7 Hz)	1.11 (t, J = 3 Hz)	6.41 (t, J = 7 Hz) 7.03 (t, J = 7 Hz) 7.33 (d, J = 7 Hz)	−12.3 (s)
7	–	–	−0.28 (t, J = 5 Hz)	0.93 (qui, J = 7 Hz) 1.76 (m)	6.85–7.18 (Ph) [e]	18.6 (s)
8	1643	3425	−0.24 (t, J = 5 Hz)	1.05 (qui, J = 7 Hz) 2.00 (m)	6.64 (s, NH) 7.02–7.30 (Ph) [e]	20.4 (s)
9	1610	3424	0.25 (dd, J = 2 and 8 Hz)	1.44 (d, J = 9 Hz) 1.49 (d, J = 11 Hz) 1.44–1.56 (m, CH_2) 1.75–1.87 (m, CH_2)	6.76 (t, J = 8 Hz) 7.13 (t, J = 8 Hz) 7.42 (d, J = 8 Hz) 7.53 (s, NH)	25.3 (d) and 39.6 (d) (J(P–P) = 22 Hz)
10	1632	–	−0.26 (t, J = 6 Hz)	1.03 (qui, J = 8 Hz) 1.75 (m)	1.48–1.71 (m) 3.57–4.00 (m)	20.1 (s)
11	1547	–	−0.08 (t, J = 7 Hz)	1.20 (t, J = 3 Hz)	1.33 (br) 3.24 (br)	−11.0 (s)
12	1548	–	−0.26 (t, J = 6 Hz)	1.86 (t, J = 3 Hz)	1.13 (br) 2.97 (br)	15.4 (s)
13	1588	–	0.40 (dd, J = 3 and 8 Hz)	1.9–2.5 (m, CH_2)	1.36 (br) 3.30 (br)	33.3 (d) and 59.8 (d) (J(P–P) = 25 Hz)
14	1538	–	−0.09 (t, J = 7 Hz)	1.20 (t, J = 3 Hz)	0.92 (t, J = 7 Hz) 3.07 (q, J = 7 Hz)	−11.4 (s)
15	1559	–	0.41 (dd, J = 2 and 8 Hz)	2.0–2.4 (m, CH_2)	1.03 (t, J = 7 Hz) 3.20 (q, J = 7 Hz)	37.8 (d) and 64.1 (d) (J(P–P) = 23 Hz)
16 [d]	1613	2616 (ν(O–H))	−0.24 (t, J = 6 Hz)	1.07 (qui, J = 8 Hz) 2.00 (m)	12.25 (br, OH)	20.0 (s)

[a] KBr disk. [b] In CD_2Cl_2, at 100 MHz. Chemical shifts are referred to Me_4Si as an external standard. [c] In CD_2Cl_2, at 40 MHz. Chemical shifts are referred to 85% H_3PO_4 as an external standard. [d] Hydrogencarbonate complex (see text). [e] Exact chemical shifts and coupling constants are obscure due to overlap with the signals of phenyl group in the phosphine ligands.

for **11–15** are given in the Experimental section. The Pd–Me group in the complexes with monodentate ligands (**6–8, 10–12, 14** and **16**) appeared as a triplet in the ^{1}H NMR spectrum (^3J(P–H) = 5–7 Hz). The P–CH_3 signals of the PMe_3- and $PMePh_2$-coordinated complexes (**6, 11, 12,** and **14**) and the P–CH_2–CH_3 signals of the PEt_2Ph-coordinated complexes (**7, 8, 10,** and **16**) were found as a triplet and a quintet, respectively. These coupling patterns of Pd–Me and methyl groups of phosphine ligands are consistent with the *trans* configuration of the square planar complexes. The Pd–Me group in the carbamate complexes with bidentate phosphine ligands (**9, 13,** and **15**) was observed as a doublet of doublets, showing the *cis* configuration.

In the IR spectrum of carbamate complexes, strong absorption due to the ν(C=O) band was observed in the range 1648–1538 cm^{-1}. The hydrogen carbonate complex (**16**) showed characteristic bands at 2616 cm^{-1} due to ν(O–H) and at 1613 and 1354 cm^{-1} due to $\nu(OCO_2)$. The low frequency of ν(O–H) absorption indicates a dimeric structure for **16**, in which two [$PdMe(OCOOH)(PEt_2Ph)_2$] units are associated by hydrogen bonds. A similar structure also involving hydrogen bonds was confirmed for $[PdMe(OCOOH)(PEt_3)_2]_2$ by X-ray analysis [5,7].

The value of ν(C=O) absorption for the carbamate complexes bearing an alkyl-substituted amino group (**11–15**) (1538–1588 cm^{-1}) is too low for the monodentate carbamate structure but may be consistent with the bidentate or bridging coordination mode. In order to make the proper structural assignment, X-ray diffraction study of complex **14** was attempted. Slow cooling of an Et_2O-hexane solution of **14**, however, gave single crystals of the dimeric compound $Pd_2Me_2(\mu\text{-}OCONEt_2)_2(PMe_3)_2$ (**17**), suitable for X-ray analysis, instead of the crystals of **14**. Compound **17** may be formed by dimerization of $[PdMe(OCONEt_2)(PMe_3)]$ species, generated by the dissociation of PMe_3 ligand from **14**. Figure 1 depicts the structure of **17**. Bond distances and angles are listed in Table 3. The two palladium centers are linked by bridging carbamate ligands. The Pd1–Pd2 distance is 3.058(1) Å, this value indicating no direct metal–metal interaction.

TABLE 3. Bond distances (Å) and angles (deg) for $Pd_2Me_2(OCONEt_2)_2(PMe_3)_2$ (**17**)

Bond distances					
Pd1–Pd2	3.058(1)	Pd1–C1	2.10(2)	Pd1–P1	2.203(4)
Pd1–O2	2.19(1)	Pd1–O4	2.125(9)		
Pd2–C2	2.05(2)	Pd2–P2	2.200(4)	Pd2–O1	2.08(1)
Pd2–O3	2.13(1)	P1–C3	1.80(2)	P1–C4	1.78(3)
P1–C5	1.91(3)	P2–C6	1.82(3)	P2–C7	1.84(3)
P2–C8	1.80(2)	C9–O1	1.26(2)	C9–O2	1.25(2)
C9–N1	1.40(2)	N1–C10	1.47(3)	N1–C12	1.44(3)
C10–C11	1.50(5)	C12–C13	1.52(4)	C14–O3	1.24(2)
C14–O4	1.30(2)	C14–N2	1.37(2)	N2–C15	1.55(3)
N2–C17	1.43(2)	C15–C16	1.50(4)	C17–C18	1.53(4)
Bond angles					
C1–Pd1–P1	88.2(5)	C1–Pd1–O2	169.9(6)		
C1–Pd1–O4	85.3(5)	P1–Pd1–O2	94.5(3)		
P1–Pd1–O4	173.0(3)	O2–Pd1–O4	91.4(4)		
Pd1–P1–C3	121.8(8)	Pd1–P1–C4	117.8(9)		
Pd1–P1–C5	112.5(6)	C3–P1–C4	101.0(1.2)		
C4–P1–C5	100.9(1.2)	C3–P1–C5	99.4(1.2)		
Pd2–P2–C6	112.6(9)	Pd2–P2–C7	115.1(7)		
Pd2–P2–C8	118.6(9)	C6–P2–C7	104.7(1.2)		
C7–P2–C8	103.4(1.0)	C6–P2–C8	100.7(1.3)		
Pd1–O2–C9	126.8(1.0)	Pd2–O1–C9	123.7(1.0)		
O1–C9–O2	125.5(1.4)	O2–C9–N1	118.1(1.4)		
O1–C9–N1	116.2(1.3)	C9–N1–C10	120(2)		
C9–N1–C12	119.1(1.4)	C10–N1–C12	121(2)		
N1–C10–C11	109(2)	N1–C12–C13	109(2)		
Pd1–O4–C14	119.8(8)	Pd2–O3–C14	125.3(9)		
O3–C14–O4	127.2(1.2)	O3–C14–N2	118.2(1.2)		
O4–C14–N2	114.2(1.2)	C14–N2–C15	120.0(1.3)		
C14–N2–C17	121(2)	C15–N2–C17	119(2)		
N2–C15–C16	110(2)	N2–C17–C18	111(2)		

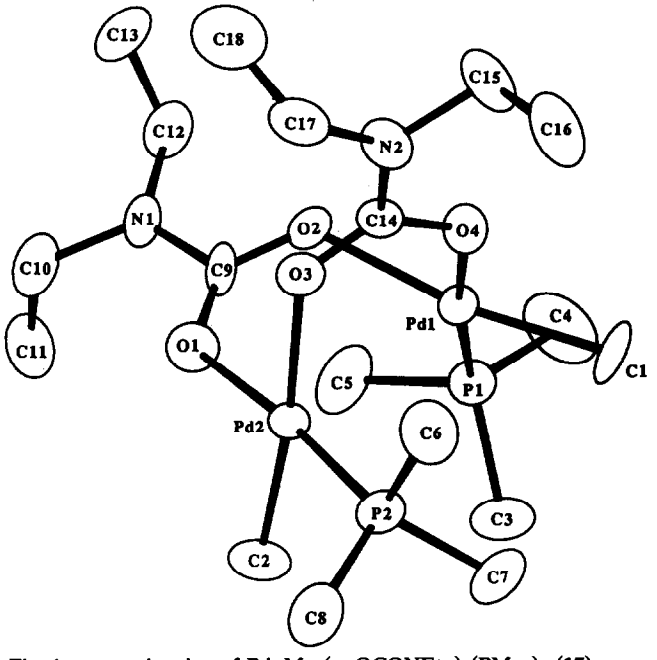


Fig. 1. ORTEP drawing of $Pd_2Me_2(\mu\text{-}OCONEt_2)_2(PMe_3)_2$ (17).

TABLE 4. Atomic coordinates with equivalent isotropic temperature factors for $Pd_2Me_2(\mu\text{-}OCONEt_2)_2(PMe_3)_2$ (17)

Atom	x	y	z	B_{eq} [a]
Pd1	0.55653(6)	0.16740(6)	0.45275(9)	3.40
Pd2	0.44905(6)	0.29245(6)	0.31338(9)	3.51
P1	0.5367(3)	0.0417(2)	0.3751(4)	4.51
P2	0.3413(2)	0.3184(3)	0.4300(4)	4.90
O1	0.5430(7)	0.2692(8)	0.1905(10)	5.3
O2	0.6378(6)	0.2130(6)	0.3122(10)	4.5
O3	0.5398(6)	0.3705(6)	0.3998(10)	4.7
O4	0.5746(7)	0.2812(6)	0.5477(9)	4.3
N1	0.6739(10)	0.2353(10)	0.1242(12)	5.5
N2	0.6111(10)	0.4183(8)	0.5552(14)	5.6
C1	0.4985(13)	0.1219(11)	0.6046(14)	6.0
C2	0.3648(11)	0.2251(13)	0.213(2)	6.2
C3	0.4324(13)	−0.005(2)	0.363(3)	8.2
C4	0.595(2)	−0.0446(14)	0.433(3)	9.2
C5	0.571(2)	0.0373(12)	0.216(2)	8.0
C6	0.370(2)	0.390(2)	0.548(2)	8.7
C7	0.2962(11)	0.225(2)	0.502(2)	7.5
C8	0.2494(13)	0.371(2)	0.372(3)	8.7
C9	0.6144(11)	0.2368(9)	0.2142(13)	4.4
C10	0.650(2)	0.265(2)	0.008(2)	7.5
C11	0.611(3)	0.193(3)	−0.059(3)	9.0
C12	0.7573(13)	0.202(2)	0.146(2)	7.0
C13	0.820(2)	0.275(2)	0.153(3)	11.2
C14	0.5753(8)	0.3534(8)	0.4934(12)	3.6
C15	0.647(2)	0.4022(10)	0.678(2)	6.7
C16	0.582(3)	0.423(2)	0.769(3)	8.4
C17	0.6179(13)	0.5011(10)	0.507(2)	7.2
C18	0.701(2)	0.511(2)	0.439(3)	11.5

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j[U_{ij}(a_i^* a_j^*)(\mathbf{a}_i \cdot \mathbf{a}_j)] = (4/3)\Sigma_i\Sigma_j[\beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)]$.

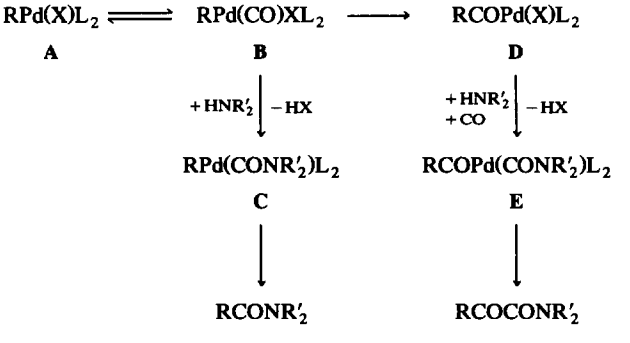
2.2. *Carbonylation of methylpalladium amide and carbamate complexes*

Methylpalladium carbamate complexes with alkyl-substituted amino groups (**11**, **12**, **14** and **15**) underwent decarboxylative carbonylation to give α-keto amides and amides as double and single carbonylation products in good to modest yields (eqn. (3)) (Table 5, entries 1, 2, 4 and 5). The selectivity for formation of α-keto amide was much higher in the reactions with monodentate phosphine complexes (**11**, **12** and **14**) than in that with the bidentate phosphine complex **15**. Addition of basic amine (piperidine) to the system effectively increased the yield of α-keto amide (entry 3). In this case, the carbonylation products exclusively involved the amino group originated from the added amine. Compound **8** with the less basic amino group (NHPh) did not form carbonylation product in the absence of added amine but afforded α-keto amide in good yield in the presence of piperidine (entry 6).

$$PdMe(OCONRR')L_2 + CO \xrightarrow{-CO_2} MeCOCONRR' + MeCONRR' \quad (3)$$

In the previous study, we proposed the reaction mechanism in Scheme 2 for formation of α-keto amide and amide from organopalladium species (**A**) [4]. The amide formation involves an organo(carbamoyl)palladium intermediate (**C**) generated by nucleophilic attack of amine to a carbonyl species (**B**). On the other hand, in the α-keto amide formation, the organocarbonyl species (**B**) undergoes CO-insertion to give an acylpalladium complex (**D**). Further interaction of **D** with CO and amine gives an acyl-carbamoyl intermediate (**E**), which reductively eliminates α-keto amide. Similar mechanisms have been also proposed by Sen [8], Tanaka [9], and Chen [10].

In the present reaction (eqn. (3)), coordination of CO to the palladium center of the carbamate complex is considered to accelerate the decarboxylation of the carbamate group with liberation of the amide entity.



Scheme 2. Proposed mechanism for formation of amide and α-keto amide from organopalladium complex.

$$MePd(OCONRR')L_2 \xrightarrow{+CO} \underset{\displaystyle CO}{\underset{|}{MePd(OCONRR')L_2}} \xrightarrow{-CO_2} MePd(CONRR')L_2$$

Scheme 3.

The amide entity thus released will immediately attack the coordinated CO ligand to give carbamoyl complex as illustrated in Scheme 3. Reductive elimination of the carbamoyl group with methyl or acetyl group formed by CO-insertion into the Pd–Me bond will produce amide or α-keto amide as shown in Scheme 2. Addition of more basic amine than the amino unit in the original carbamate ligand yields the amide or α-keto amide containing the amide entity derived from the added amine. In this case, the added amine will effectively compete with the original amide entity to give the carbamoyl ligand of the more basic amine and release the amide or α-keto amide of the amine added to the system.

Treatment of the diphenylamide complexes with carbon monoxide gave diphenylamine as the major product. For example, the reaction of **6** with CO (10 atm) in benzene at room temperature for 10 min gave diphenylamine in 79% yield together with a small amount of N,N-diphenylacetamide (7%) (eqn. (4)). We did not pursue the source of the proton which gave the diphenylamine.

$$\underset{\textbf{6}}{\textit{trans}\text{-}PdMe(NPh_2)(PMe_3)_2} + \underset{(10\ atm)}{CO} \xrightarrow[benzene]{room\ temp.} Ph_2NH + MeCONPh_2 \quad (4)$$

(79%) (7%)

2.3. Synthesis of methylpalladium alkyl carbonate complexes

In connection with the chemistry of methylpalladium carbamate complexes, we prepared some methylpalladium alkyl carbonate complexes for comparison and studied their behavior.

$$PdMe_2L_2 + HOR \xrightarrow[Et_2O,\ room\ temp.]{CO_2} PdMe(OCOOR)L_2 + CH_4 \quad (5)$$

18: L = PMe_3, R = Me

19: L = PMe_3, R = ^{s}Bu

20: L = PPh_3, R = Me

The methylpalladium alkyl carbonate complexes were prepared by treating the dimethylbis(tertiary phosphine) palladium complexes with alcohols in the presence of carbon dioxide and characterized by elemental analysis and IR and NMR spectroscopy (see Experimental section). This reaction is considered to proceed in a manner similar to the reactions of the dimethylpalladium complexes with carbon dioxide and amines, for which protonolysis of the dimethyl complexes with carbamic acid was proposed. Also in the reactions with carbon dioxide and alcohols, it is probable that the reactions proceed by protonolysis of the dimethylpalladium complexes with alkylcarbonic acid generated by the reaction of carbon dioxide with alcohol as illustrated below.

$$HOR + CO_2 \rightleftharpoons HOCOOR \quad (6)$$

$$PdMe_2L_2 + HOCOOR \longrightarrow PdMe(OCOOR)L_2 + CH_4 \quad (7)$$

In comparison to the methyl(carbamate)palladium complexes, the alkyl carbonate complexes having PMe_3 and PPh_3 ligands showed lower reactivity towards carbon monoxide. At room temperature they did not react with carbon monoxide even under the CO pressure of 20 or 30 atm, but they gave modest ($\approx$ 30% for **18**) to good ($\approx$ 60% for **20**) yields of methyl acetate at 80–100°C under CO pressure of 30 atm in benzene or toluene solutions. Further increase in the CO pressure did not improve the yields of methyl acetate. No double carbonylation product (α-keto ester) was detected.

3. Experimental section

3.1. General

All manipulations were carried out under an atmosphere of argon, nitrogen or carbon monoxide or *in vacuo*. ^1H, ^{13}C and ^{31}P NMR spectra were measured on JEOL FX-100, GX-270 and GX-500 spectrometers by Dr. Y. Nakamura, Ms. R. Ito, and Ms. A. Kajiwara in our laboratory. ^1H and ^{13}C signals are referred to Me_4Si as an internal standard and ^{31}P NMR signals to 85% H_3PO_4 as an external reference. IR spectra were recorded on a JASCO IR-810 spectrometer. Mass spectrometry was performed with a Hitachi M-80 GC-mass spectrometer. Elemental analysis was carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory with a Yanagimoto CHN autocorder type MT-2. Solvents and amines were dried in the usual ways, distilled, and stored under an argon atmosphere. Carbon dioxide (Nippon Sanso) was dried by passage through concentrated H_2SO_4. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. Dimethylpalladium complexes (**1–5**) were prepared as reported [11].

3.2. Preparation of trans-PdMe(NPh$_2$)(PEt$_2$Ph)$_2$ (7)

To a Schlenk tube (*ca.* 50 ml) containing *trans*-PdMe$_2$(PEt$_2$Ph)$_2$ (**2**) (211 mg, 0.45 mmol) were added Et$_2$O (10 ml) and diphenylamine (189 mg, 1.12 mmol) at room temperature. The system was evacuated and carbon dioxide (1 atm) was introduced. The mixture was stirred at room temperature for 24 h. The initially colorless solution turned yellow. Solvent was pumped out and the resulting oily material dissolved in acetone at room temperature. The acetone solution was cooled to −78°C to give a yellow crystalline solid of **7**, which was filtered, washed with cold Et$_2$O and dried under vacuum (168 mg, 60%).

Similarly obtained was *trans*-PdMe(NPh$_2$)(PMe$_3$)$_2$ (**6**, 68%), which was recrystallized from Et$_2$O.

3.3. Preparation of trans-PdMe(OCONEt$_2$)(PMe$_3$)$_2$ (14)

To a homogeneous colorless solution of *trans*-PdMe$_2$(PMe$_3$)$_2$ (**1**) (110 mg, 0.38 mmol) in Et$_2$O (5 ml) was added Et$_2$NH (0.96 mmol) at room temperature. The system was evacuated and carbon dioxide was introduced. The mixture was stirred at room temperature for 51 h to give a pale yellow solution, which was concentrated to dryness by pumping to give a yellowish solid. The crude product was washed with hexane and dried under vacuum to give a colorless solid of **14** (135 mg, 75%). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −13.3 (t, J(P–C) = 3 Hz, Pd*C*H$_3$), 12.5 (t, J(P–C) = 13 Hz, P*C*H$_3$), 13.0 (s, NCH$_2$*C*H$_3$), 41.0 (s, N*C*H$_2$), and 161.4 (s, *C*O).

Similarly obtained were **8** (62%), **9** (43%), **10** (30%), **11** (41%), **12** (43%), **13** (55%), and **15** (63%). Recrystallization of the complexes was carried out by using the following solvents: CH_2Cl_2-Et$_2$O (**8** and **12**), CH_2Cl_2-hexane (**9**, **13** and **15**), acetone (**10**), and Et$_2$O (**11**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): (**11**) δ −13.1 (t, J(P–C) = 7 Hz, Pd*C*H$_3$), 12.5 (t, J(P–C) = 14 Hz, P*C*H$_3$), 25.0 and 26.4 (both s, NCH$_2$*C*H$_2$*C*H$_2$), 45.6 (s, N*C*H$_2$), and 161.6 (s, *C*O); (**12**) δ −7.3 (t, J(P–C) = 4 Hz, Pd*C*H$_3$), 12.5 (t, J(P–C) = 13 Hz, P*C*H$_3$), 25.0 and 26.0 (both s, NCH$_2$*C*H$_2$*C*H$_2$), 45.2 (s, N*C*H$_2$), and 161.3 (s, *C*O); (**13**) δ 10.0 (dd, J(P–C) = 4 and 99 Hz, Pd*C*H$_3$), 23.4 (dd, J(P–C) = 11 and 26 Hz, P*C*H$_2$), 29.8 (dd, J(P–C) = 23 and 33 Hz, P*C*H$_2$), 24.9 and 26.2 (both s, NCH$_2$*C*H$_2$*C*H$_2$), 45.6 (s, N*C*H$_2$), and 161.6 (s, *C*O); (**15**) δ 10.0 (J(P–C) = 2 and 95 Hz), 23.5 (dd, J(P–C) = 14 and 20 Hz, P*C*H$_2$), 29.8 (dd, J(P–C) = 24 and 35 Hz, P*C*H$_2$), 14.3 (s, NCH$_2$*C*H$_3$), 41.3 (s, N*C*H$_2$), 161.4 (s, *C*O).

3.4. Preparation of trans-PdMe(OCOOH)(PEt$_2$Ph)$_2$]$_2$ (16)

To a Schlenk tube containing an Et$_2$O solution (5 ml) of *trans*-PdMe$_2$(PEt$_2$Ph)$_2$ (**2**) (216 mg, 0.46 mmol) was added Ph(Me)NH (1.17 mmol) at room temperature. The system was evacuated by pumping and CO_2 gas (1 atm) was introduced. After the mixture was stirred for 24 h at room temperature, the solvent was removed by pumping, and the resulting white solid was recrystallized from acetone to give a white crystalline solid of **16** (80%).

3.5. X-Ray diffraction study of Pd$_2$Me$_2$(μ-OCONEt$_2$)$_2$-(PMe$_3$)$_2$ (17)

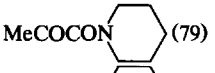
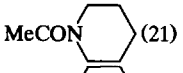
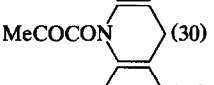
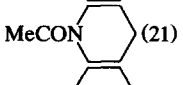
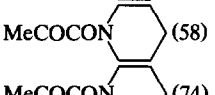
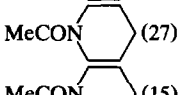
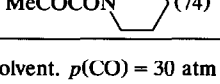
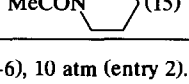
A solution of *trans*-PdMe(OCONEt$_2$)(PMe$_3$)$_2$ (**14**) in Et$_2$O was diluted with hexane (1/1 ratio) and allowed to stand at −20°C for 2 days to give white crystals (18% yield). The elemental analysis suggested the composition of [PdMe(OCONEt$_2$)(PMe$_3$)], where one of the PMe$_3$ ligands in **14** was lost during the recrystallization. Anal. Calcd for $C_9H_{22}NO_2PPd$: C, 34.5; H, 7.1; N, 4.5. Found: C, 34.4; H, 7.0; N, 4.2%. A single crystal of dimensions *ca.* 0.20 × 0.30 × 0.35 mm was sealed in a glass capillary tube under argon, and subjected to X-ray diffraction study.

Crystal data: Formula, $C_{18}H_{44}N_2O_4P_2Pd_2$, M = 627.31; orthorhombic, a 15.712(2), b 15.818(3), c 11.526(8) Å; V 2864.7(8) Å^3; D_c = 1.47 g cm^{-3}; Z = 4; space group, $P2_12_12_1$; μ(Mo Kα) = 13.71 cm^{-1}; F(000) = 320.

Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ 0.71068 Å). Unit cell dimensions and an orientation matrix were obtained by a least-squares calculation for 25 automatically centred reflections in the range $20 \leq 2\theta \leq 25°$. Diffraction intensities were measured at 19°C in the range $3 \leq 2\theta \leq 55°$ ($0 < h < 19$, $0 < k < 20$, $0 < l < 13$) using ω–2θ scan technique at a scan rate of 8°/min. Three standard reflections, measured at every 100 reflection measurements, showed no appreciable decrease in the intensities during the data collection. No absorption correction was made. Of the 3647 unique reflections measured, 3131 were classed as observed ($F_o > 3\sigma(F_o)$) and these were used for the solution and refinement of the structure.

Calculations were performed on a FACOM A-70 computer using the R-CRYSTAN program. The structure was solved by a combination of direct methods (SAPI85) and Fourier techniques. Hydrogen atoms were not located. The structure was refined by full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. The final R value was 0.064 (R_w = 0.080) ($w = [(F_o)^2 + 0.069\sigma(F_o)^2]^{-1}$). The selected bond distances and angles are listed in Table 3. Fractional coordinates and equivalent isotropic thermal parameters are given in Table 4. Tables of anisotropic thermal parameters and observed and cal-

TABLE 5. Reaction of methylpalladium carbamate complexes with carbon monoxide [a]

Entry	Complex	Additive (equiv./Pd)	Product (yield, %/Pd)	
1	**14**	–	$MeCOCONEt_2$ (12)	$MeCONEt_2$ (26)
2	**15**	–	$MeCOCONEt_2$ (< 1)	$MeCONEt_2$ (64)
3	**14**	piperidine (1)	 (79)	 (21)
4	**11**	–	 (30)	 (21)
5	**12**	–	 (58)	 (27)
6	**8**	piperidine (1)	 (74)	 (15)

[a] The reaction was carried out on a 0.05–0.1 mmol scale using 3 ml of solvent. $p(CO) = 30$ atm (entries 1, 3–6), 10 atm (entry 2). Solvent: THF (entries 1, 3–6), benzene (entry 2). Reaction temperature: 100°C (entries 1, 3–6), room temperature (entry 2).

culated structure factors are available from the authors.

3.6. Preparation of *trans*-PdMe(OCOOMe)(PMe_3)$_2$ (18)

Into the heterogeneous mixture of *trans*-$PdMe_2(PMe_3)_2$ (0.74 mmol) and Et_2O (6 ml), methanol (8.88 mmol) was added at −78°C under a nitrogen atmosphere. The atmosphere of the reaction system was replaced with carbon dioxide and the system was stirred at room temperature for 1 day. From the colorless solution thus obtained, the solvent was removed by evacuation and the remaining solid was recrystallized from a mixture of CH_2Cl_2 and hexane to give a white crystalline compound of **18** in 70% yield. IR (KBr): 1647 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2, −40°C): δ 0.05 (t, $J = 7$ Hz, 3H, PdCH_3), 1.21 (t, $J = 3$ Hz, 18H, PCH_3), 3.40 (s, 3H, OCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ −12.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ −12.4 (t, $J = 7$ Hz, PdCH_3), 12.3 (t, $J = 14$ Hz, PCH_3), 53.1 (s, OCH_3), 158.4 (s, CO). Anal. Calcd for $C_9H_{24}O_3P_2Pd$: C, 30.9; H, 7.1. Found: C, 31.0; H, 6.9%.

Similarly obtained were *trans*-PdMe(OCOOMe)(PPh_3)$_2$ (**19**, 58%) and *trans*-PdMe(OCOO^s-Bu)(PMe_3)$_2$ (**20**, 62%). (**19**) IR (KBr): 1641 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2, −40°C): δ −0.23 (t, $J = 6$ Hz, 3H, PdCH_3), 2.70 (s, 3H, OCH_3), 7.15–7.93 (m, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ 29.8 (s). Anal. Calcd for $C_{39}H_{36}O_3P_2Pd$: C, 65.0; H, 5.0. Found: C, 64.6; H, 5.1%. (**20**) IR (KBr): 1656 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2, −40°C): δ −0.04 (t, $J = 7$ Hz, 3H, PdCH_3), 0.80 (t, $J = 7$ Hz, 3H, OCH(CH_3)(CH_2CH_3)), 1.05 (d, $J = 7$ Hz, 3H, OCH(CH_3)CH_2CH_3), 1.22 (t, $J = 3$ Hz, 18H, PCH_3), 1.30–1.49 (m, 2H, CH(Me)(CH_2CH_3)), 4.25 (q, $J = 6$ Hz, 1H, CH(CH_3)(CH_2CH_3)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ −12.0 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ −12.7 (t, $J = 6$ Hz, PdCH_3), 10.2 (s), 12.3 (t, $J = 13$ Hz, PCH_3), 20.2 (s), 29.3 (s), 72.2 (s), 157.8 (s, CO). Anal. Calcd for $C_{12}H_{30}O_3P_2Pd$: C, 36.9; H, 7.7. Found: C, 36.7; H, 7.9%.

3.7. Carbonylation reaction

Methylpalladium carbamate or amide complex (0.05–0.1 mmol) was placed in a stainless steel pressure bottle under a nitrogen atmosphere, and solvent (THF or benzene) and/or piperidine were added. CO gas (30 or 10 atm) was introduced, and the system was heated at 100°C with stirring for 1 day. After the CO gas was purged, the resulting red reaction solution was examined by GLC (PEG 20M (2 m) or Silicon OV-1 (2 m)) using Ph_2O as an internal reference. The results of reactions are listed in Table 5.

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