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Chemistry of diamino-ligated methylpalladium(II) alkoxides and aryloxides (Part II): methoxide formation and carbonylation reactions [1]

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Abstract

Reaction of N-ligated methylpalladium(II) alkoxide and aryloxide complexes [Pd(Me)(OR)(N ~ N)] (R = Ph, $CH(CF_3)_2$; N ~ N = tmeda (*N,N,N',N'*-tetramethylethylenediamine) or bpy (2,2'-bipyridyl)) with carbon monoxide produces the corresponding methylesters in high yields. The insertion takes place either into the Pd–Me bond (aryloxide complexes) or into the Pd–OR bond (alkoxide complexes). Methylpalladium(II) methoxide complexes [Pd(Me)(OMe)(N ~ N)] (N ~ N = tmeda, bpy) have been generated in situ by aryloxide– or alkoxide–methanol exchange reactions for which the equilibrium constants have been determined. The bpy-ligated methylpalladium methoxide complex undergoes insertion of CO producing either a methylpalladium methoxycarbonyl complex [Pd(Me)(CO_2Me)(bpy)] (at −60°C) or an acylpalladium methoxycarbonyl complex [Pd(COMe)(CO_2Me)(bpy)] (at −25°C); both carbonylated species could be isolated and characterized at low temperature.

Keywords: Palladium; Alkoxides; Aryloxides; Diamino; Methoxycarbonyl; Acyl; Carbonylation

1. Introduction

Reported interesting properties of late transition metal alkoxides include C–O bond formation [2], association with alcohols to form adducts through O–H · · · O hydrogen bonding [3], and β-hydrogen elimination from the alkoxide ligand to release aldehydes or ketones [4]. Another intriguing feature of late transition metal alkoxides is their ability to insert small molecules (such as carbon monoxide) into the metal-to-oxygen bond. The latter reaction is one of the key steps in a number of palladium-catalyzed processes [5].

Alkylmetal alkoxides and aryloxides have two possible pathways for migratory CO insertion and these involve insertion of CO into the metal–carbon bond or, alternatively, insertion into the metal–oxygen bond. Subsequent reductive elimination of a carboxylic ester is possible from the insertion intermediate that results from either pathway. It is known that carbonylation of methylnickel(II) and methylpalladium(II) aryloxide complexes generates the corresponding acyl complexes by preferential migratory insertion of CO into the M–C bond rather than into the M–O bond, and acylnickel and acylpalladium complexes such as [M(COMe)(OC_6H_4-CN-4)(PEt_3)$_2$] (M = Ni, Pd) have been successfully isolated from such reactions at low temperature [6]. Upon heating, the latter palladium(II) complex cleanly liberates the ester $MeCO_2C_6H_4$CN-4. In the case of acylnickel(II) aryloxides, the reductive elimination of the ester must be assisted by addition of π-acids such as CO or olefins [6]. The corresponding methylnickel(II) and methylpalladium(II) alkoxides also react with carbon monoxide to afford the corresponding methyl esters [7]; however, the intermediates involved are different from those with aryloxide ligands. Reaction of [Pd(Me)($OCH(CF_3)_2$)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) with an equimolar amount of CO at −60°C shows insertion into the Pd–O bond to form an

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[1] For Part I, see Ref. [1].

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alkoxycarbonyl complex [Pd(Me)($CO_2CH(CF_3)_2$)-(dppe)], which at higher temperatures liberates the corresponding ester [7]. Recently, Tóth and Elsevier reported the reaction of CO with P-ligated methylpalladium methoxides to form methylpalladium(II) methoxycarbonyl species and suggested a non-concerted associative pathway for this reaction [8]. In contrast to palladium chemistry, there are several reports on the insertion of CO into a Pt–OMe bond to produce thermally stable methoxycarbonyl complexes. For example, reaction of CO with [Pt(Me)(OMe)(dppe)] produced [Pt(Me)(CO_2Me)(dppe)] and the latter complex showed no tendency to undergo reductive elimination [9]. The mechanism proposed for the latter reaction was described as an inner-sphere migratory insertion involving pre-coordination of CO to the metal center [9]. More interestingly, multiple carbonylations have also been reported for alkylmetal alkoxides. While [Pt(C_6H_9)-(OMe)(dppe)] inserts CO only into the Pt–O bond, the dppp (= 1,3-bis(diphenylphosphino)propane) analogue inserts CO both into the Pt–O bond (25°C, very fast) and the Pt–C bond (50°C, slow) [10]. This dichotomy in the chemistry of alkylmetal alkoxides and aryloxides towards CO (i.e. insertion into either the M–C or M–O bond or into both) is intriguing and merits further investigation.

In the course of our study concerning palladium alkoxide complexes [11], we recently studied the synthesis and properties of methylpalladium alkoxides of the type [Pd(Me)(OR)(N ~ N)] in which N ~ N is a bidentate N-donor ligand such as *N,N,N′,N′*-tetramethylethylenediamine (tmeda) or 2,2′-bipyridyl (bpy). These complexes showed interesting properties such as O–H · · · O hydrogen bonding to produce alcohol adducts and exchange of coordinated alkoxide for associated alcohol (see part I; Ref. [1]). Almost simultaneously, another group reported the synthesis of tmeda-ligated palladium(II) alkoxides [12]. The use of bidentate N-donor ligands leads to Pd–C and Pd–O bonds that are stronger than those in related P-donor ligated complexes studied by Yamamoto and co-workers [3a,c,d]. The availability of the N-ligated complexes [Pd(Me)(OR)-(N ~ N)] prompted us to study the reactivity of both the Pd–O and Pd–C bond towards carbon monoxide so that we could compare the reactivity of analogous N- and P-ligated complexes. Some aspects of the carbonylation of these species was communicated earlier [13].

2. Experimental section

2.1. General procedures

Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Methanol (p.a.) and Celite (filter aid) were purchased from Janssen Chimica. ^{1}H (300.13 MHz) and ^{13}C NMR (75.04 MHz) spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature in NMR solvents (CD_3OD, $CDCl_3$, CD_2Cl_2 and CD_3COCD_3) obtained from ISOTEC Inc. Infra-red spectra (K Br discs) were recorded on a Perkin Elmer 283. Organic products were analyzed by GLC using a Varian system with a silica-coated capillary column and by GC-MS using a Unicam 610 Automass System. The complexes [Pd(Me)(OCH-(CF_3)$_2$)(tmeda)] (**1**) [1,12], [Pd(Me)-(OPh)(tmeda)] (**2**) [1,12], [Pd(Me)($OCH(CF_3)_2$)(bpy)] (**3**) [1] and [Pd(Me)(OPh)(bpy)] (**4**) [1] were prepared according to literature procedures.

2.2. Reaction of methylpalladium alkoxide and aryloxide complexes 1–4 with carbon monoxide

The alkylpalladium alkoxide or phenoxide complex **1–4** (15 mg) was dissolved in $CDCl_3$ (1 ml) at room temperature and CO (1 atm) was introduced. The yellow solution turned colorless with the formation of Pd(0). After 30 min of stirring, quantitative GLC analysis (diphenylmethane as internal standard) of the filtered solution showed the formation of 1,1,1,3,3,3-hexafluoro-2-propyl acetate or phenyl acetate respec-

Table 1
Yields of esters from the carbonylation of methylpalladium alkoxide and aryloxide complexes [a]

Entry	Complex	Solvent	Ester	Yield (%)	Ref.
Alkoxide complexes					
1	[Pd(Me)($OCH(CF_3)_2$)(tmeda)]	acetone	$MeCOOCH(CF_3)_2$	98	this work
2	[Pd(Me)($OCH(CF_3)_2$)(bpy)]	acetone	$MeCOOCH(CF_3)_2$	98	this work
3	[Pd(Me)($OCH(CF_3)$(Ph))(PMe_3)$_2$] [b]	Et_2O	$MeCOOCH(CF_3)$(Ph)	99	[6a]
4	[Pd(Me)($OCH(CF_3)_2$)(dppe)]	THF	$MeCOOCH(CF_3)_2$	68	[10]
Aryloxide complexes					
5	[Pd(Me)(OPh)(tmeda)]	acetone	MeCOOPh	70	this work
6	[Pd(Me)(OPh)(bpy)]	acetone	MeCOOPh	71	this work
7	[Pd(Me)(OPh)(PMe_3)$_2$] [b]	CH_2Cl_2	MeCOOPh	16	[6a]
8	[Pd(Me)(OPh)(dppe)]	toluene	MeCOOPh	trace	[6a]

[a] Reactions were carried out under an atmosphere of excess CO (1 atm). Yields were determined by GLC analysis with diphenylmethane as an internal standard or integration in ^{1}H NMR. The formation of carboxylic esters was also confirmed by IR. [b] *Trans* isomer.

tively (see Table 1). The formation of the esters was also quantified by ^{1}H NMR and identified by IR spectroscopy.

2.3. Carbonylation of methylpalladium alkoxide and aryloxide complexes 1 and 2 in the presence of secondary amines

The methylpalladium alkoxide or phenoxide complex **1–4** (15 mg) was dissolved in acetone (4 ml) at room temperature and an exact amount (see Table 2) of HNR'_2 (R' = Et or ^{i}Pr) was added and CO (1 atm) was introduced. The yellow solution turned colorless with the formation of Pd(0). After 30 min of stirring, GC-MS analysis of the filtered solution showed the formation of $MeCONR'_2$ and $MeCOCONR'_2$ and GLC analysis (diphenylmethane as internal standard) was used to quantify the formation of these products and $MeCO_2R$. Owing to its volatility the ester $MeCO_2CH(CF_3)_2$ is particularly difficult to quantify, and this was done in only one case where the total conversion was high.

2.4. In situ formation of [Pd(Me)(OCD$_3$)(N ~ N)] (N ~ N = tmeda (5-d_3) and bpy (6-d_3)). Determination of the equilibrium constant for alkoxide / aryloxide–methanol exchange

An exact amount of **1–4** (ca. 15.0 mg) was dissolved in CD_3OD (0.500 ml). ^{1}H NMR spectroscopy showed the formation of the methoxide complexes, [Pd(Me)-(OCD_3)(N ~ N)] (N ~ N = tmeda (**5**-d_3) or bpy (**6**-d_3)) in equilibrium with the starting material. The tmeda-ligated methoxide complex **5**-d_3 can be generated starting from complexes **1** or **2** and the bipyridine methoxide complex **6**-d_3 from **2** or **3**. The equilibrium constant K_{eq} for this reaction was determined at five different temperatures through use of ^{1}H NMR spectroscopy with integral values of the Pd–Me resonances. ^{1}H NMR (CD_3OD) **5**-d_3: δ 2.64–2.48 (m, 4H, CH_2), 2.54 (s, 6H, NMe_2), 2.50 (s, 6H, NMe_2), 0.34 (s br, 3H, Pd–CH_3). ^{1}H NMR (CD_3OD) **6**-d_3: δ 8.72 (s br, 1H, H_6), 8.65 (d, 1H, $^3J_{H,H}$ = 6 Hz, $H_{6'}$), 8.37 (d, 2H, $^3J_{H,H}$ = 7 Hz, H_3 and $H_{3'}$), 8.12 (t, 2H, $^3J_{H,H}$ = 7 Hz, H_4, $H_{4'}$), 7.69 (t, 1H, $^3J_{H,H}$ = 6 Hz, H_5), 7.59 (t, 1H, $^3J_{H,H}$ = 7 Hz, $H_{5'}$), 0.86 (s br, 3H, Pd–CH_3). ^{13}C NMR (CD_3OD) **5**-d_3: δ 64.36 (CH_2), 58.60 (CH_2), 51.38 (NMe_2), 47.43 (NMe_2), −1.78 (br, Pd–CH_3). ^{13}C NMR (CD_3OD) **6**-d_3: 158.7, 154.4, 151.2, 148.9, 140.6, 140.2, 127.8, 127.7, 124.5, 123.2 (bpy carbon-skeleton), 2.50 (br, Pd–CH_3). Owing to the fact that CD_3OD was used, the palladium methoxide signal was not observed in the ^{1}H and ^{13}C NMR spectra.

2.5. Reaction of the methylpalladium methoxide complexes 5-d_3 and 6-d_3 with CO. In situ formation of the methoxycarbonyl complexes [Pd(Me)(CO_2CD_3)(N ~ N)] (N ~ N = tmeda (7-d_3) and bpy (8-d_3))

Carbon monoxide was bubbled through a pre-cooled (−78°C) solution of the fluorinated alkoxide palladium complexes **1** or **3** (ca. 15 mg) in CD_3OD (0.5 ml) which also contained the palladium methoxide complexes **5**-d_3 and **6**-d_3. ^{1}H NMR spectra taken in the temperature range −78 to 20°C showed the formation of the methoxycarbonyl complexes [Pd(Me)(CO_2CD_3)(N ~ N)] (N ~ N = tmeda) (**7**-d_3) or bpy (**8**-d_3)). Above 0°C decomposition started and organic products together with Pd(0) were formed. ^{1}H NMR (CD_3OD, 213 K) **7**-d_3: δ 3.15–3.07 (m, 2H, CH_2), 2.30–2.21 (m, 2H, CH_2), 2.53 (s, 6H, NMe_2), 2.42 (s, 6H, NMe_2), −0.19 (s, 3H, Pd–CH_3). ^{1}H NMR (CD_3OD, 213 K) **8**-d_3: δ 8.58 (s br, 2H, H_6), 8.46 (s br, 2H, H_3), 8.17 (s br, 2H, H_4), 7.72 (s br, 2H, H_5), 0.34 (s, 3H, Pd–CH_3). ^{13}C NMR (CD_3OD:$C_6D_5CD_3$ v:v = 1:1; 213 K) **7**-d_3: δ 205.50 (CO), 61.10 (CH_2), 59.43 (CH_2), 52.25 (br, NMe_2), 46.64 (br, NMe_2), 1.23 (Pd–CH_3). ^{13}C NMR (CD_3OD:$C_6D_5CD_3$ v:v = 1:1; 213 K) **8**-d_3: 208.55, (CO), 156.29, 154.56, 151.37, 148.40, 140.23, 139.82, 127.50, 127.14, 123.93, 123.79 (bpy skeleton), 16.25 (Pd–CH_3).

2.6. Synthesis of [Pd(Me)(CO_2Me)(bpy)] (8)

The fluorinated alkoxide complex **2** (0.38 g, 0.84 mmol) was dissolved in MeOH (20 ml) and cooled to

Table 2
Products from the carbonylation of methylpalladium alkoxide and aryloxide complexes [Pd(Me)(OR)(tmeda)] in the presence of dialkylamines [a]

Entry	R	Amine [b]	$MeCONR'_2$ (%)	$MeCOCONR'_2$ (%)	MeCOOR (%)
1	Ph (**2**)	$HNEt_2$ (1)	46	20	30
2	Ph (**2**)	$HNEt_2$ (10)	54	41	< 1
3	Ph (**2**)	HN^iPr_2 (10)	19	0	25
4	$CH(CF_3)_2$ (**1**)	$HNEt_2$ (1)	50	20	24
5	$CH(CF_3)_2$ (**1**)	$HNEt_2$ (10)	59	36	[c]
6	$CH(CF_3)_2$ (**1**)	HN^iPr_2 (1)	2	0	89

[a] Reactions in acetone with CO at atmospheric pressure (see Experimental for details). Yields determined by GLC analysis with diphenylmethane as an internal standard. [b] Between parentheses are the equivalents of amine used relative to the palladium complex. [c] Not measured, but must be less than 5%.

−60°C. Carbon monoxide was bubbled through this solution and within 5 min a yellow precipitate formed. The suspension was allowed to warm to −50°C and the solid was isolated by centrifugation and decantation at this temperature, washed with cold Et_2O (less than −30°C, 3 × 10 ml) and dried in vacuo. Yield 0.22 g (78%). ^1H NMR (CD_2Cl_2, 243 K): δ 8.55 (d, 1H, $^3J_{H,H}$ = 6 Hz, H_6), 8.46 (d, 1H, $^3J_{H,H}$ = 6 Hz, H_6), 8.16 (d, 1H, $^3J_{H,H}$ = 7 Hz, H_3), 8.13 (d, 1H, $^3J_{H,H}$ = 7 Hz, H_3), 8.01 (t, 1H, $^3J_{H,H}$ = 7 Hz, H_4), 7.96 (t, 1H, $^3J_{H,H}$ = 7 Hz, H_4), 7.49 (t, 1H, $^3J_{H,H}$ = 6 Hz, H_5), 7.43 (t, 1H, $^3J_{H,H}$ = 6 Hz, H_5), 3.60 (s, 3H, Pd–CO_2CH_3), 0.32 (s, 3H, Pd–CH_3). ^{13}C NMR (CD_2Cl_2, 243 K): δ 196.54 (*CO*), 155.08, 152.28, 150.61, 147.65, 138.90, 138.43, 126.54, 125.87, 122.14, 121.94 (bpy skeleton), 49.61 (OCH_3), −8.41 (Pd–CH_3). IR (KBr): ν(CO) 1630 cm^{-1}.

2.7. Synthesis of [Pd(Me)(CO_2CD_3)(bpy)] (8-d_3)

The synthesis follows a procedure identical to that for the non-deuterated analogue **8** but employing CD_3OD instead of MeOH. Yield 0.20 g (70%). ^1H NMR (CD_2Cl_2, 243 K): identical to **8** with the exception of the absence of methoxycarbonyl proton resonances. ^{13}C NMR (CD_2Cl_2, 243 K): identical to **8** except for the absence of the Pd–OMe resonance. IR (KBr): ν(CO) 1630 cm^{-1}.

2.8. Synthesis of [Pd(COMe)(CO_2Me)(bpy)] (9)

The fluorinated alkoxide complex **2** (0.15 g, 0.33 mmol) was dissolved in MeOH (10 ml) and the solution cooled to −30°C. Carbon monoxide was bubbled through the solution at this temperature for 5 min and a yellow precipitate formed. The suspension was allowed to warm to −20°C, after which the solid was isolated by centrifugation and decantation at this temperature and then washed with cold Et_2O (less than −30°C, 3 × 10 ml) and dried in vacuo. Yield 0.15 g (51%). ^1H NMR (CD_2Cl_2, 243 K): δ 8.53 (d, 1H, $^3J_{H,H}$ = 6 Hz, H_6), 8.23 (d, 1H, $^3J_{H,H}$ = 6 Hz, H_6), 8.20 (d, 1H, $^3J_{H,H}$ = 7 Hz, H_3), 8.10 (d, 1H, $^3J_{H,H}$ = 7 Hz, H_3), 8.00 (t, 1H, $^3J_{H,H}$ = 7 Hz, H_4), 7.98 (t, 1H, $^3J_{H,H}$ = 7 Hz, H_4), 7.36–7.32 (m, 2H, H_5), 3.52 (s, 3H, OCH_3), 2.40 (s, 3H, $COCH_3$). ^{13}C NMR (CD_2Cl_2, 243 K): δ 246.80 (*C*OMe), 192.31 (CO_2Me), 153.70, 152.89, 150.50, 150.14, 139.29, 139.21, 126.17, 126.01, 122.40, 122.16 (bpy skeleton), 48.71 (CO_2CH_3), 42.22 (Pd–$COCH_3$). IR(KBr): ν(CO) 1641, 1620 cm^{-1}.

2.9. Reaction of [Pd(Me)(CO_2Me)(bpy)] (8) with carbon monoxide

The methoxycarbonyl complex **8** (0.15 g, 0.44 mmol) was suspended in MeOH (10 ml) at −25°C and carbon monoxide was then bubbled through the suspension for 1 h at this temperature. The suspension was allowed to warm to −20°C, after which the yellow precipitate which had formed was isolated by centrifugation and decantation and then washed with cold Et_2O (less than −30°C, 2 × 10 mL) and dried in vacuo. ^1H and ^{13}C NMR in CD_2Cl_2 (−30°C) showed this material to be a mixture of the methylpalladium methoxycarbonyl complex **8** (25%) and acylpalladium methoxycarbonyl complex **9** (75%).

3. Results

3.1. Carbonylation of methylpalladium alkoxide and aryloxide complexes

The N-donor ligated methylpalladium(II) alkoxides [Pd(Me)($OCH(CF_3)_2$)(N ~ N)] (N ~ N = tmeda, **1**; bpy, **2**) and aryloxides [Pd(Me)(OPh)(N ~ N)] (N ~ N = tmeda, **3**; bpy, **4**) [1], react with carbon monoxide (1 atm) in non-alcoholic solvents (acetone) at room temperature to produce the corresponding methyl esters 1,1,1,3,3,3-hexafluoro-2-propyl acetate and phenyl acetate respectively, with simultaneous formation of the free diamine ligand (N ~ N) and palladium black:

$$[Pd(Me)(OR)(N \sim N)] \xrightarrow[\text{acetone}]{CO} MeCOOR + N \sim N + Pd^{\circ} \quad (1)$$

1: R = $CH(CF_3)_2$; N ~ N = tmeda

2: R = Ph; N ~ N = tmeda

3: $CH(CF_3)_2$; N ~ N = bpy

4: Ph; N ~ N = bpy

When complexes with the fluorinated alkoxide ligand are used in this carbonylation the reaction is fast (less than 5 min) and the yield of the corresponding methyl ester is quantitative (see Table 1). However, with the phenoxide ligand complexes the reaction takes longer (more than 15 min) to convert the starting material completely and, furthermore, one obtains a lower yield of the ester than in the case of alkoxide ligand complexes.

3.2. Carbonylation of methylpalladium alkoxide and aryloxide complexes in the presence of dialkylamines

The single or double carbonylation of alcohols and/or amines is of importance for the synthesis of several classes of organic compounds, like α-ketoamides and their derivatives [14]. To improve these catalytic transformations it is relevant to understand the mechanism, such as the order of CO migratory insertion into a metal–acyl or metal–alkyl bond. Our N-ligated

methylpalladium alkoxides give us the opportunity to investigate the different reactivity of Pd–O and Pd–C bonds towards CO and amines and to compare the results with those from related P-ligated complexes. In a carbonylation procedure similar to that described in the previous section, but now in the presence of dialkylamines (HNR'_2) methylpalladium alkoxide and aryloxide complexes [Pd(Me)(OR)(tmeda)] (R = $CH(CF_3)_2$, **1**; Ph, **2**) produce α-keto-amide $MeCOCONR'_2$ and amide $MeCONR'_2$, as well as the ester $MeCO_2R$:

$$[Pd(Me)(OR)(N \sim N)] \xrightarrow[2.\ CO]{1.\ HNR'_2} MeCONR'_2 + MeCOCONR'_2 + N \sim N + Pd^{\circ} \quad (2)$$

1: $CH(CF_3)_2$; N ~ N = tmeda

2: Ph; N ~ N = tmeda

The ratio of the products, α-keto-amide/amide, depends upon the amount and type of dialkylamine present (see Table 2). In all cases there is less of the α-keto-amide than the amide and, with $HN(^iPr)_2$, formation of the double carbonylation product becomes negligible.

The formation of methyl esters during these reactions can be, to all intents and purposes, suppressed when excess dialkylamine is used; this results in increased yields of the amide and α-keto-amide (see entries 1 and 2, Table 2).

3.3. Formation of methylpalladium(II) methoxide complexes

When [Pd(Me)(OR)(tmeda)] (R = $CH(CF_3)_2$, **1**; Ph, **2**) or [Pd(Me)(OR)(bpy)] (R = $CH(CF_3)_2$, **3**; Ph, **4**) are dissolved in CD_3OD the ^1H NMR spectrum shows some new resonances in addition to signals arising from unreacted **1**–**4**. For example, dissolution of **1** (or **2**) in CD_3OD affords a new Pd–Me signal (δ = 0.34 ppm), a new set of tmeda resonances and signals from free $HOCH(CF_3)_2$ (or HOPh). The dissolution of **3** (or **4**) in CD_3OD produces similarly a new Pd–Me signal at δ = 0.88 ppm and a new set of bpy resonances. These data are consistent with the in situ formation of new methylpalladium methoxide complexes formulated, as depicted in Fig. 1, as [Pd(Me)(OCD_3)(N ~ N)] (N ~ N = tmeda, **5**-d_3; bpy, **6**-d_3).

It was possible to determine the equilibrium constant

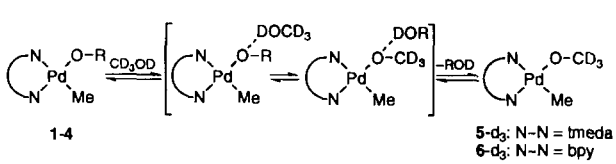

Fig. 1. Formation of methylpalladium methoxide complexes.

Table 3
Equilibrium constants for alkoxide- or aryloxide–methanol exchange of [Pd(Me)(OR)(N ~ N)] [a]

R	N ~ N	$-\log K_{eq}$	$-\log K_{cal}$
$CH(CF_3)_2$	tmeda	2.1	6.2
$CH(CF_3)_2$	bpy	2.5	6.2
Ph	tmeda	4.0	5.5
Ph	bpy	4.5	5.5

[a] $-\log K_{cal} = pK_a(MeOH) - pK_a(HOR)$ with pK_a values for methanol, phenol and $HOCH(CF_3)_2$ of 15.5, 10.0 and 9.3 respectively.

K_{eq} for these alkoxide- or aryloxide–methanol exchange reactions by variable-temperature NMR experiments (see Experimental) and the results are included in Table 3; the calculated equilibrium constants K_{cal} for the reaction of an alkoxide anion with an alcohol, based upon the acidity constants pK_a of MeOH and the corresponding alcohol ROH, are also tabulated.

From the NMR spectroscopic data it was apparent that K_{eq} was invariant to changes in starting conditions such as temperature (290–340 K) and concentration of the alkoxide (or phenoxide) complex (5–70 mg Pd complex in 0.50 ml CD_3OD). Furthermore, the values of K_{eq} for these exchange reactions show that the equilibrium lies almost completely to the side of the starting complex and, therefore, in order to achieve a significant concentration of complexes **5**-d_3 or **6**-d_3, a large excess of CD_3OD is needed.

The dimethylpalladium(II) complex [$Pd(Me)_2$(bpy)] does not react with MeOH to afford the corresponding methylpalladium methoxide, and the starting materials can be recovered unchanged. A similar result was reported for P-ligated dimethylpalladium complexes [3a]. However, this method of reacting an alkylpalladium species with an alcohol does work for more acidic alcohols (such as fluorinated or aryl alcohols) with P- or N-donor ligated dimethylpalladium complexes and it affords methylpalladium alkoxides [1,3,12]. The use of methanol is more successful in platinum chemistry; for example, reaction of N-ligated dimethylplatinum(II) or P-ligated platinum(0) complexes with MeOH leads to platinum(IV) [15] and platinum(II) methoxide complexes [16] respectively.

3.4. Carbonylation of methylpalladium(II) methoxide complexes

We have also explored whether it was possible to react the in situ generated methoxide complexes [Pd(Me)(OCD_3)(N ~ N)] (N ~ N = tmeda, **5**-d_3; bpy, **6**-d_3) with CO and to actually isolate carbonylated species. Equilibrium mixtures in CD_3OD of the methylpalladium 1,1,1,3,3,3,-hexafluoro-2-propoxide complex **1** or **3** and the newly formed methylpalladium methox-

ide complexes, containing as neutral ligand either tmeda (**5**-d_3) or bpy (**6**-d_3), react with CO at −50°C in $CD_3OD1C_6D_5CD_3$ to afford, as the exclusive CO-containing product, the corresponding methylpalladium methoxycarbonyl complex [Pd(Me)(CO_2CD_3)(N ~ N)] (N ~ N = tmeda(**7**-d_3); bpy (**8**-d_3)). The ^{1}H NMR spectra show the Pd–Me signal for **7**-d_3 and **8**-d_3 at −0.19 and 0.34 ppm respectively, which is in both cases 0.54 ppm to higher field than these resonances in the methoxopalladium complexes **5**-d_3 and **6**-d_3. These data are consistent with the conversion of the cis OCD_3 ligand in **5**-d_3 and **6**-d_3 to CO_2CD_3 in **7**-d_3 and **8**-d_3.

By bubbling CO through a solution of [Pd(Me)-($OCH(CF_3)_2$)(bpy)] (**3**) in a minimum of MeOH at −60°C the methyl(methoxycarbonyl) complex [Pd-(Me)(CO_2Me)(bpy)] (**8**) precipitated (see Fig. 2); this complex has been isolated at low temperatures as a yellow solid in high yield. Unfortunately, it has not proved possible to obain a good elemental analysis for **8** because it decomposes slowly over a few hours even at low temperature; this complex has been identified unambiguously by spectroscopic methods. In the ^{13}C NMR spectrum of **8** (CD_2Cl_2, 243 K) the carbonyl carbon resonance is at 196.5 ppm and this value is similar to that of 201.9 ppm found for the corresponding carbon atom in [Pd(Me)($CO_2CH(CF_3)_2$)(dppe)] (CD_2Cl_2, 213 K) [7]. A solid state IR spectrum of complex **8** showed the presence of a strong CO stretching vibration at 1630 cm^{-1}, which is in good agreement with the ν(CO) of 1633 cm^{-1} for [Pd(CO_2Me)$_2$(bpy)] [17]. In this carbonylation reaction of **3** to afford **8** there was no evidence found for the presence of acylpalladium methoxide species which could result from insertion of CO into the Pd–Me bond. Remarkably, even though the solution comprises an equilibrium mixture of the fluorinated alkoxide and the methoxide palladium complexes in a molar ratio of approximately 1:1, no products arising from insertion of CO into the Pd–$OCH(CF_3)_2$ bond were found. The formation of **8** indicates that insertion into the Pd–OMe bond is kinetically preferred with respect to insertion into either the Pd–Me or the Pd–$OCH(CF_3)_2$ bond. Obviously, the conversion of the methoxide complex **6**-d_3 into a methoxycarbonyl complex drives the alkoxide-methanol exchange equilibrium completely to the side of the palladium methoxide complex and, therefore, the methoxycarbonyl complex can be generated quantitatively starting from the equilibrium mixture. The isolation of [Pd(Me)(CO_2CD_3)-(bpy)] (**8**) with bpy as the N-donor ligand shows the importance of using the correct ligands for stabilizing such methylpalladium methoxycarbonyl complexes. In this context it is worth noting that Tóth and Elsevier reported the in situ generation at low temperature (−50°C) of a related phosphine-ligated methoxycarbonyl complex [Pd(Me)(CO_2Me){(*S*,*S*)-bdpp}] ((*S*,*S*)-bdpp = (2*S*,*S*)-2,4-bis(diphenylphosphino)pentane) [8].

When CO is bubbled through a solution of [Pd(Me)($OCH(CF_3)_2$)(bpy)] (**3**) in MeOH at −25°C, in a procedure similar to that used for obtaining **8** at −60°C, an acyl(methoxycarbonyl) complex [Pd(CO-Me)(CO_2Me)(bpy)] (**9**) is formed (see Fig. 2); this has been isolated at low temperature as an orange solid in 43% yield. The ^{13}C NMR spectrum of **9** (CD_2Cl_2, 243 K) shows the carbonyl-type carbon atom resonances at 192.3 and 246.8 ppm which, in combination with a signal at 42.22 ppm, points to the presence of an acylpalladium unit; such units have expected $\delta(^{13}C)$ values of ca. 250–210 ppm ($COCH_3$) and ca. 45–30 ppm ($COCH_3$) [18]. Furthermore, the $\delta(^{13}C)$ value of 192.3 ppm for the CO_2CH_3 unit in **9** is similar to that of 196.5 ppm found for this unit in [Pd(Me)(CO_2Me)-(bpy)] (**8**). By bubbling CO through a solution of **8** in MeOH at −25°C it was also possible to generate [Pd(COMe)(CO_2Me)(bpy)] (**9**) (see Fig. 2), and after 15 min the conversion of **8** into **9** was ca. 75%.

4. Discussion

4.1. Formation of N-ligated palladium methoxide complexes

In CD_3OD solutions the palladium methoxide complexes [Pd(Me)(OCD_3)(N ~ N)] (N ~ N = tmeda, **5**-d_3; bpy, **6**-d_3) show a remarkable stability which is probably due to the formation of adducts of the type [Pd(Me)(OCD_3)(N ~ N)] · $HOCD_3$ involving O–H · · · O interactions (see Fig. 1). We, and others, have

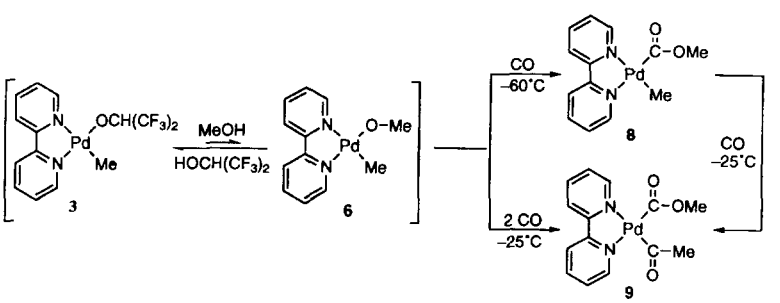

Fig. 2. Carbonylation of methylpalladium methoxide complexes.

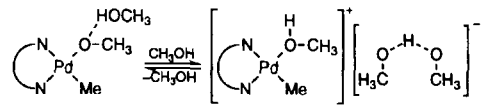

Fig. 3. Formation of cationic palladium species in methanol.

reported several stable alcohol adducts in palladium alkoxide chemistry in which the hydrogen-bond stabilizes the Pd–O interaction [1,3,12a]. For example, we recently reported the molecular structure of the N-ligated palladium aryloxide adducts [Pd(Me)(OPh)(tmeda)] · HOPh and [Pd(Me)(OC_6H_4X-4)(tmeda)] · HOC_6H_4X-4 [1]. It has been suggested that the stability of palladium methoxides in methanol could in fact arise from intermolecular exchange between coordinated methoxide and the methanol solvent, with this process being faster than β-hydrogen elimination from the Pd–OCH_3 unit [4a,c]. Another factor that could contribute to the stability of the methoxide species **5**-d_3 and **6**-d_3 is that the alcohol adducts could disproportionate in this polar medium to produce ionic species $[Pd(Me)(HOCD_3)(N \sim N)]^+$ $[CD_3O \cdots H \cdots OCD_3]^-$ (see Fig. 3); similar species have been reported for Ru–OR complexes [3d,h].

The formation of such cationic palladium complexes is more likely for N-ligated complexes like **5** and **6** than for related P-ligated palladium alkoxides, since the RO^- ligand trans to nitrogen has a higher negative charge and, therefore, becomes a better leaving group. Our experimental results seem to corroborate this idea, since we were only able to obtain NMR data of **5**-d_3 and **6**-d_3 in CD_3OD; in other solvents (such as C_6D_6 or $CDCl_3$) we encountered decomposition.

The measured equilibrium constants for the exchange of coordinated aryloxide groups for methanol (Table 3) reveal them to be comparable with the pK_a difference of the applied alcohols. However, the alkoxide–methanol equilibrium is shifted more to the side of palladium methoxide than can be expected on the basis of the pK_a differences of the alcohols used. This indicates that, for alkoxide ligands, the acidity of the alcohol is not a good tool for predicting the K_{eq} for the exchange reaction and that probably other factors, such as bond dissociation energies of H–OR [19] and X–H $\cdots$ O hydrogen bonding (X = C, O) [1], play a role. Alkoxide–alcohol exchange reactions of this type have been reported before for transition-metal alkoxide complexes, and it has been suggested that an associative mechanism is operative [1,5c,19]. Thermodynamic parameters for alkoxide/aryloxide–methanol exchange in our species have not been obtained since K_{eq} in this system changes very little with the temperature.

4.2. Mechanism for CO insertion reactions

Our present results show that carbonylation of N-ligated methylpalladium aryloxide complexes produces better yields of methyl esters than the corresponding P-donor ligated aryloxide complexes (Table 1, entries 5–8), which is probably due to the lability of the Pd–Me interaction trans to nitrogen. It is interesting to see that our carbonylation reactions of N-ligated methylpalladium alkoxides in the presence of secondary amines produces high yields of mono and double carbonylated products, whereas the reported carbonylation of the P-ligated complex *trans*-[Pd(Me)(OPh)($PEt_2Ph)_2$] in the presence of Et_2NH produced only low yields of $MeCONEt_2$ (15%) and $MeCOCONEt_2$ (25%) [18a], even though the reactions conditions (p_{CO} = 10 atm; 1 day) were more severe than those we applied. On the basis of our results, and those from P-donor ligated methylpalladium alkoxide complexes, it is clear that the selectivity for α-keto-amide formation is difficult to control, but it is evident that polar solvents direct the reaction more to the double carbonylated product. We conclude that cationic palladium species probably play an important role in the mechanism that leads to double carbonylation of amines, since a species $[Pd(Me)(HOCD_3)(N \sim N)]^+[CD_3O \cdots H \cdots OCD_3]^-$ would be particularly susceptible to incoming nucleophiles such as carbon monoxide.

In the reaction of CO with N-ligated methylpalladium alkoxide and aryloxide complexes, a remarkable difference is found both in the yields of methyl ester and in the comparative reaction rates; we believe that this could be due to the occurrence of different operative reaction pathways. It is likely that the aryloxide palladium complexes react with CO via migratory insertion of CO into the Pd–Me bond rather than into the Pd–OAr bond, whereas alkoxide ligands undergo preferential migratory insertion of CO into the Pd–O bond rather than into the Pd–Me bond [3a,6–10]. It has been suggested previously that the low reactivity of methylpalladium aryloxides towards CO may be due to their reluctance to undergo the CO insertion into the Pd–Me bond rather than into the Pd–OAr bond [3a]. We believe that the migratory insertion of CO into either the Pd–C or Pd–OR bond is the rate determining step in these carbonylation reactions, and that this is responsible for the observed differences in reactivity for alkoxide and aryloxide ligands. The subsequent C–C bond forming step to form the methyl ester is assumed to be fast, although the nature of the species undergoing this reductive elimination is very different. On the one hand it is a reductive elimination of an acyl/aryloxide pair, and on the other hand a methyl/alkoxycarbonyl combination. Yamamoto and co-workers studied the carbonylation of the related P-ligated methylpalladium complexes of the type [Pd(Me)(OR)L_2] and found the same remarkable difference between the alkoxide and aryloxide complexes (see Table 1) [3a,17].

The mechanism of CO insertion into late transition-metal alkoxide bonds is currently a subject of discussion

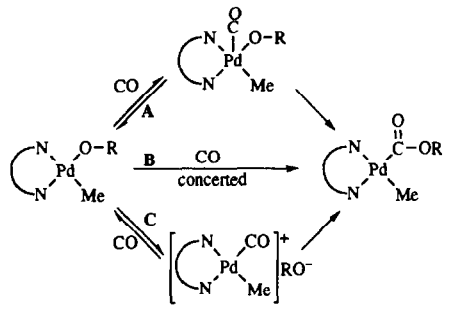

Fig. 4. Mechanisms for insertion of CO into a Pd–O bond.

in the literature. To describe the formation of late transition-metal alkoxycarbonyl complexes (see Fig. 4), the following pathways have frequently been put forward: (i) pre-coordination of CO followed by migratory insertion into the Pd–O bond (associative, pathway A) [5c,9]; (ii) an unprecedented insertion of CO into the Pd–O bond (concerted, pathway B) [5c]; (iii) displacement of RO^- by CO to form cationic carbonyl complexes followed by nucleophilic attack of the alkoxide anion on coordinated CO (dissociative, pathway C) [5c,8b].

From our studies on N-ligated palladium alkoxides it is not possible to distinguish between these mechanisms, but we strongly favor route C for N-ligated methylpalladium alkoxides, since we believe that N-donor ligands will favor the dissociation of the methylpalladium methoxides to cationic palladium methanol complexes (vide supra).

The proposed mechanism for the reaction of methylpalladium alkoxides with CO in the presence of secondary amines is shown in Fig. 5.

In order to produce amides and α-keto-amides the first step in the reaction mechanism must involve insertion of CO into the Pd–Me bond to produce acylpalladium alkoxide intermediates [14,18]. Nucleophilic attack of HNR'_2 on the coordinated acyl unit of the latter complex would then lead to liberation of the corresponding amide. An alternative to nucleophilic attack of the amine involves the reaction of the acylpalladium

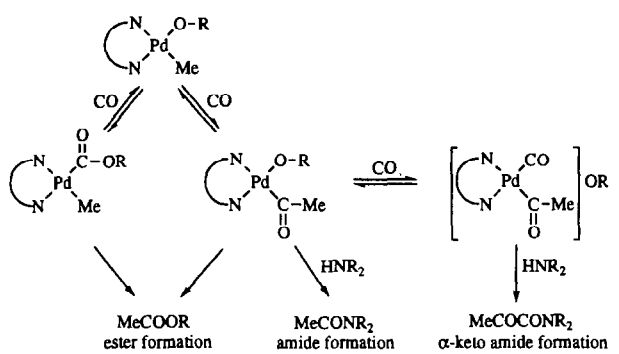

Fig. 5. Single and double carbonylation mechanism for methylpalladium alkoxides.

alkoxide with another equivalent of CO to form an ionic species. Ozawa et al. provided evidence for the existence of such ionic intermediates, since polar solvents and/or alkoxide ligands containing the more electron-withdrawing groups produce higher yields of α-keto-amide [18]. Reaction of the ionic intermediate with the dialkylamine would give an acylpalladium carbamoyl intermediate, and subsequent reductive elimination of acyl and carbamoyl groups from this intermediate would give $MeCOCONR'_2$.

An alternative pathway for α-keto-amide formation involves double insertion of CO into the Pd–Me bond to produce Pd–COCOMe intermediates; this is followed by nucleophilic attack of the amine on the latter species to produce α-keto-amides. Yamamoto provided evidence against this mechanism, since treatment of $[Pd(COCOMe)(Cl)(PMePh_2)_2]$ (which is prepared by oxidative addition of RCOCOCl to a Pd(0) complex) with Et_2NH gives the amide $MeCONEt_2$ as the major product [20]. This is in sharp contrast with the reaction of the corresponding acyl complex $[Pd(COMe)(Cl)(PMePh_2)_2]$ with Et_2NH under a CO atmosphere which produced the α-keto-amide $MeCOCONEt_2$ as the major product [20]. Furthermore, it is clear from these reactions that the bulk of the amine plays a crucial role in the formation of double carbonylated products [21], since with HN^iPr_2 no α-keto-amides are produced.

5. Concluding remarks

The present study of aryloxide and alkoxide methylpalladium complexes reveals that analogous N- and P-ligated complexes do have a different reactivity towards CO, and that subsequent yields of ester from N-ligated complexes are higher. The initial carbonylation of methylpalladium alkoxides and aryloxides follow different reaction paths (insertion into either Pd–OR or Pd–Me respectively) and, furthermore, carbonylation of methylpalladium(II) methoxides can take place either into the Pd–OMe bond or into both the Pd–Me and Pd–OMe bonds (depending upon the temperature) to produce rare examples of isolable methylpalladium(II) or acylpalladium(II) methoxycarbonyl species. This basic knowledge may be useful in helping elucidate reaction mechanisms of some metal-catalyzed reactions (possible intermediates in methoxycarbonylation reactions) as well as in the development of new synthetic organic reactions.

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