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Protonation and alkylation of benzoyl(carbamoyl)-palladium(II) and -platinum(II) complexes to give cationic benzoyl complexes with *O*-protonated and *O*-alkylated carbamoyl ligands. Characterization of an intermediate in the reaction of *trans*-[Pd(COPh)(CO)(PMe_3)$_2$]BF_4 with pyrrolidine to give *trans*-Pd(COPh)(CON$(CH_2)_3CH_2$)(PMe_3)$_2$

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Abstract

trans-[Pd(COPh)(CO)(PMe_3)$_2$]BF_4 (**1**) reacts with pyrrolidine to afford a cationic benzoylpalladium(II) complex with an *O*-protonated carbamoyl ligand *trans*-[Pd(COPh){C(OH)(N$(CH_2)_3CH_2$)}(PMe_3)$_2$]BF_4 (**2b**), which has been characterized by means of NMR spectroscopy. Complex **2b** reacts further with pyrrolidine to give *trans*-Pd(COPh)(CON$(CH_2)_3CH_2$)(PMe_3)$_2$ (**3**) together with the pyrrolidinium salt $CH_2(CH_2)_3NH_2BF_4$. The conversion of **2b** to **3** is a reversible process, and treatment of **3** with the pyrrolidinium salt regenerates **2b**. Thermodynamic and kinetic parameters for the protonation-deprotonation equilibration between **2b** and **3** have been determined by means of NMR spectroscopy. Treatment of *trans*-Pd(COPh)(CON$(CH_2)_4CH_2$)(PMe_3)$_2$ with Et_3OBF_4 affords *trans*-[Pd(COPh){C(OEt)(N$(CH_2)_4CH_2$)}(PMe_3)$_2$]BF_4 (**4**). Ethylation of benzoyl(carbamoyl)platinum complexes *trans*- and *cis*-Pt(COPh)($CONMe_2$)(PPh_3)$_2$ with Et_3OBF_4 also gives corresponding *O*-ethylated carbamoyl complexes *trans*- and *cis*-[Pt(COPh){C(OEt)(NMe_2)}(PPh_3)$_2$]BF_4 (**5** and **6**, respectively).

Introduction

It is well documented that nucleophilic attack of amines, alcohols, and water on carbonyl ligands coordinated to transition metal complexes gives carbamoyl, alkoxycarbonyl, and hydroxycarbonyl complexes, respectively [1]. The following is a

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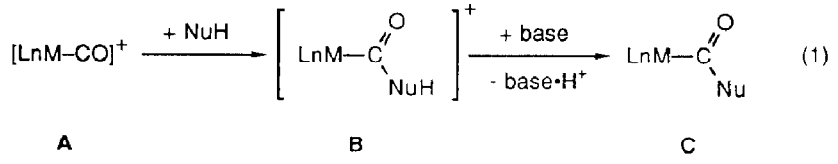
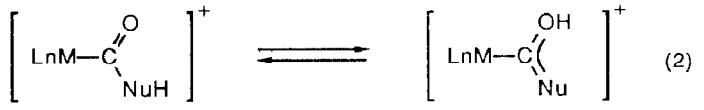
generally accepted reaction process.

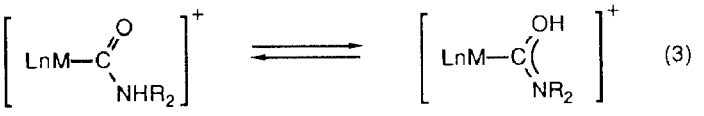


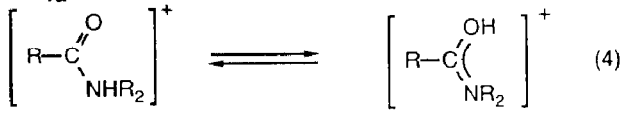
(NuH = amine, alcohol, or water)

Attack of amines, alcohols, and water, respectively on the CO ligand in **A** forms an adduct **B** which subsequently reacts with a base to give carbamoyl, alkoxycarbonyl, and hydroxycarbonyl complexes **C**. Although it is convincing that **B** serves as a key intermediate in the reactions, no direct evidence for **B** has been reported so far. Furthermore, the intermediate **B** has an isomeric structure **D** formed by proton rearrangement in the C(O)NuH ligand (eq. 2). The possibility of participation of **D** in reaction 1, however, has not been considered.

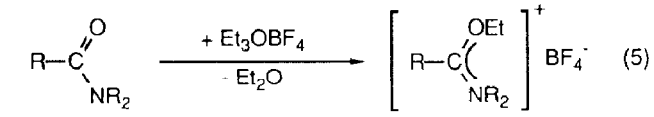


When secondary amines (R_2NH) are employed as nucleophiles in reaction 1, the intermediates **B** and **D** will have the following structures **Ia** and **Ib**, respectively. **Ia** is a cationic complex with an amine-coordinated carbonyl ligand whereas **Ib** is formally a hydroxyaminocarbene complex.

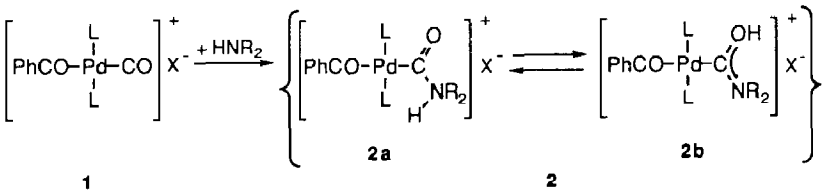




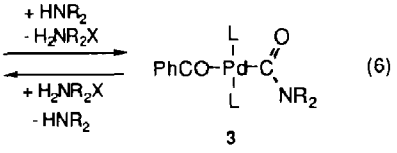
The structures **Ia** and **Ib** may be compared with those of a protonated organic amide **IIa** and **IIb**, respectively. Previous NMR studies on protonated amides have revealed that the *O*-protonated amide **IIb** is thermodynamically more stable than the *N*-protonated amide **IIa**, and both species are in rapid equilibrium on an NMR time-scale [2]. The predominant contribution of **IIb** has been supported also by the observation that reaction of amide with Et_3OBF_4 affords the *O*-alkylated amide exclusively [3].



We have recently reported in a preliminary form that reaction of *trans*-$[Pd(COPh)(CO)(PMe_3)_2]BF_4$ (**1**) with pyrrolidine forms a cationic pyrrolidine ad-



1 2a 2 2b



3 (6)

(X = BF_4, L = PMe_3, NR_2 = N⬠)

duct of benzoyl(carbonyl)palladium complex (**2**) for which the presence of tautomers **2a** and **2b** corresponding to **Ib** and **Ib** in eq. 3 is conceivable [4].

The amine adduct will give *trans*-benzoyl(carbamoyl)palladium complex (**3**) on its subsequent reaction with pyrrolidine. The carbamoyl complex thus formed regenerates the adduct **2** on its treatment with the pyrrolidinium salt. The interconversions between **1** and **2** and **2** and **3** are assumed to be important processes in the palladium-catalyzed double carbonylation of aryl halides and secondary amines to give α-keto amides [5–7].

Since complex **2** is highly temperature sensitive and readily decomposes in solution in the absence of free CO, it could not be isolated. In order to obtain further information of the structure of **2**, we prepared an alkylated analog of **2** by the reaction of *trans*-Pd(COPh)(CON$(CH_2)_4CH_2$)$(PMe_3)_2$ with Et_3OBF_4. In contrast to instability of the protonated complex **2**, the alkylated complex is stable enough to be isolated and it was examined by NMR and X-ray analysis. These studies have indicated that the alkylated complex has an *O*-ethylated carbamoyl structure *trans*-[Pd(COPh){C(OEt)(N$(CH_2)_4CH_2$)}$(PMe_3)_2$]BF_4 (**4**) corresponding to **2b** in eq. 6. We describe here full details of these results. Preparation and characterization of *trans*- and *cis*-benzoylplatinum(II) complexes with *O*-ethylated carbamoyl ligands are also reported *.

Results and discussion

Characterization of complex 2

To a CD_2Cl_2 solution of the benzoyl(carbonyl)palladium complex **1** (0.1 *M*) under CO atmosphere, 2 equivalents of pyrrolidine was added at $-40\,^{\circ}C$. The color

* The *O*-protonated and *O*-alkylated carbamoyl complexes reported in this paper are related to the well-known aminocarbene complexes of palladium(II) and platinum(II) which are prepared by the reactions of isocyanide complexes with alcohols or amines. The aminocarbene complexes are synthesized also by protonation and alkylation of iminoacylpalladium and -platinum complexes [10].

Table 1

IR and NMR data for benzoylpalladium complexes **1**, **2** and **3**

Complex	$^{13}C\{^1H\}$ NMR [a]		^1H NMR [b]		Assignment	$^{31}P\{^1H\}$ NMR [c] (ppm)	IR (cm^{-1}) [d] ν(CO)
	δ	J(P–C) [e]	δ	J(P–H) [e]			
1	14.8 (t)	16	1.31 (t, 18H)	3.9	P*Me*	−11.9 (s)	1638 (benzoyl)
	180.2 (t)	18			*C*O (terminal)		
	231.2 (br)				Ph*C*O		2138 (terminal
2	15.2 (t)	16	1.11 (t, 18H)	3.5	P*Me*	−12.0 (s)	[f]
	24.6 (s)		1.9 (br, 4H)		NCH_2CH_2		
	25.9 (s)				$NCH_2C'H_2$		
	44.3 (s)		3.2 (br, 2H)		NCH_2		
	48.6 (s)		3.8 (br, 2H)		$NC'H_2$		
	215.8 (t)	15	~8 (br, 1H)		$C(OH)(NR_2)$		
	278.1 (br)				Ph*C*O		
3	15.8 (t)	15	1.14 (t, 18H)	3.5	P*Me*	−11.7 (s)	1561 (benzoyl)
	24.8 (s)		1.8 (br, 4H)		NCH_2CH_2		
	25.8 (s)				$NCH_2C'H_2$		1518 (carbamoyl)
	43.5 (s)		3.3 (br, 2H)		NCH_2		
	47.8 (s)		3.8 (br, 2H)		$NC'H_2$		
	211.9 (t)	14			$CONR_2$		
	276.1 (t)	10			Ph*C*O		

[a] 125 MHz (**1** and **2**) or 67.8 MHz (**3**), in CD_2Cl_2, at −40 °C (**1** and **2**) or 0 °C (**3**). [b] 500 MHz (**1** and **2**) or 100 MHz (**3**), in CD_2Cl_2, at −40 °C (**1** and **2**) or room temperature (**3**). [c] 40 MHz, in CD_2Cl_2, at −50 °C; chemical shifts are relative to PPh_3 as an external standard (downfield positive). [d] In KBr disk. [e] In Hz. [f] Not measured.

of the solution instantly changed from pale yellow to bright orange. The ^{31}P and ^{13}C NMR spectra revealed formation of complex **2** in quantitative yield and absence of **1** in the system.

The NMR data of **2** are listed in Table 1 together with those of **1** and **3**. The $^{13}C\{^1H\}$ NMR spectrum exhibits two sets of triplets at δ 278.1 and 215.8, assignable to the benzoyl- and pyrrolidine-coordinated carbonyl carbons. The P-Me carbons in **2** are observed as a virtual triplet, indicating the *trans* configuration of **2**. The four carbons in the pyrrolidino group in **2** appear as non-equivalent four singlets at δ 48.6, 44.3, 25.9, and 24.6, suggesting restricted rotation around the C–N bond. This observation is consistent with the structure **2b**, in which the C–N bond possesses double-bond character, but not with **2a** with a C–N single bond.

Study on the equilibrium between 2 and 3

Addition of pyrrolidine to the NMR sample solution of **2** results in formation of the benzoyl(carbamoyl)palladium complex **3** at the expense of **2**. In the presence of 20 equiv./Pd of pyrrolidine, **2** and **3** were observed in a 1/1 ratio in the ^{31}P NMR spectrum. The relative ratio of **3** to **2** increases with an increase in the concentration of pyrrolidine in the system. The conversion of **2** into **3** is performed also by addition of Et_3N to the system. Addition of $\overline{CH_2(CH_2)_3NH_2}BF_4$ to the system, on the other hand, increases the amount of **2**. These results clearly indicate occurrence of the deprotonation-protonation equilibrium between **2** and **3** with aid of pyrroli-

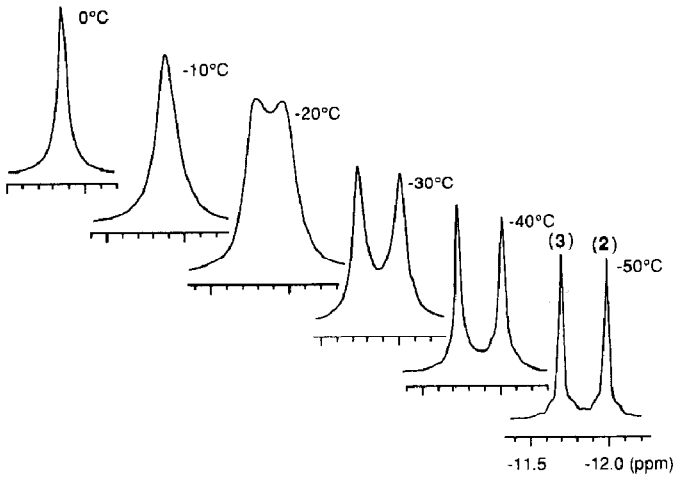
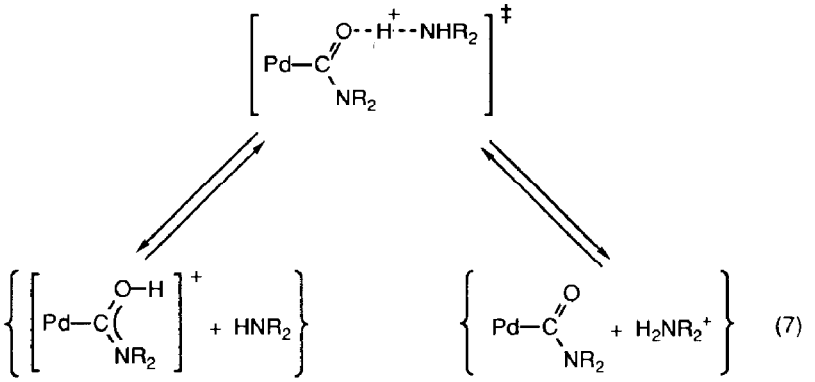


Fig. 1. Temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum (200 MHz) of a 1/1 mixture of complexes **2** and **3** in CD_2Cl_2 *.

dine and the pyrrolidinium salt as represented in eq. 6.

The interconversion between **2** and **3** is a rapid process on an NMR time-scale. Figure 1 shows temperature dependence of the ^{31}P NMR spectrum of a 1/1 mixture of **2** and **3**. At −50 °C, **2** and **3** give well-separated singlets at −12.0 and −11.7 ppm, respectively *. The signals broaden on keeping the 1/1 ratio at elevated temperatures, and coalesce into a broad singlet at ca. −15 °C. Based on the spectroscopic change in Fig. 1, the activation parameters at −15 °C for the equilibrium have been determined as follows: $\Delta H^{\ddagger} = 10.2 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -9.6 \pm 0.1$ eu, and $\Delta G^{\ddagger} = 12.6 \pm 0.1$ kcal/mol. The negative entropy may indicate an aggregated transition state.

The equilibrium constant ($K_{eq} = [\overline{CH_2(CH_2)_3NH_2}BF_4][\mathbf{3}]/[\overline{CH_2(CH_2)_3NH}][\mathbf{2}]$) for the equilibrium between **2** and **3** has been measured by ^{31}P NMR spectroscopy

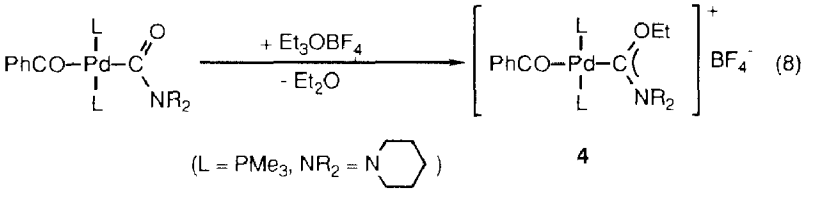


* The chemical shifts in $^{31}P\{^1H\}$ NMR spectra are relative to an external PPh_3 standard (downfield positive).

using mixtures of **2** and **3** prepared by the reactions of **1** (0.11 *M*) and five different concentrations of pyrrolidine (5–40 equiv./Pd) in CD_2Cl_2 under CO atmosphere. The equilibrium constants thus obtained were in fair agreement with each other ($K_{eq} = 0.028 \pm 0.002$). Furthermore, the K_{eq} value was scarcely affected by changing the temperature from −80 to −20 °C. Based on the equilibrium constant K_{eq} and the pK_a value (2.7) of the conjugate acid of pyrrolidine, the pK_a value of complex **2** was determined to be 12.9. This pK_a value is much higher than those of protonated organic amides (ca. −2) but is comparable to the values of alkylammonium salts.

Preparation of complex **4**

Treatment of *trans*-Pd(COPh)(CO$\overline{N(CH_2)_4CH_2}$)$(PMe_3)_2$ with an equimolar amount of Et_3OBF_4 in CD_2Cl_2 at −20 °C gives *trans*-[Pd(COPh){C(OEt)-($\overline{N(CH_2)_4CH_2}$)}$(PMe_3)_2$]BF_4 (**4**), which has been isolated as yellow crystals in 85% yield. Complex **4** has been identified as a cationic benzoylpalladium complex with an *O*-ethylated carbamoyl ligand by means of IR and NMR spectroscopy (Table 2) and by single-crystal X-ray analysis.



The IR spectrum of **4** shows two strong absorptions at 1606 and 1529 cm^{-1}. In order to assign these two bands, the ^{13}C-labeled complex *trans*-[Pd(COPh)-{^{13}C(OEt)($\overline{N(CH_2)_4CH_2}$)}$(PMe_3)_2$]BF_4 (**4**-^{13}C) was prepared from *trans*-Pd-(COPh)(^{13}CO$\overline{N(CH_2)_4CH_2}$)$(PMe_3)_2$. The absorptions at 1606 cm^{-1} was not affected by the ^{13}C-labelling whereas the other absorption at 1529 cm^{-1} shifted to 1509 cm^{-1}. Thus the former absorption at 1606 cm^{-1} is assigned to the ν(CO) band of the benzoyl group and the latter to the *O*-ethylated carbamoyl ligand. The absorption at 1509 cm^{-1} observed in the IR spectrum of **4**-^{13}C is in fair agreement with the calculated value for the asymmetric O–^{13}C–N stretching vibration (1507 cm^{-1}), but not with the values for pure ^{13}C=O and ^{13}C=N double bonds (1495 and 1497 cm^{-1}, respectively) [8]. This indicates delocalization of the π electrons over the C–N and C–O bonds, consistent with the *O*-ethylated carbamoyl structure of **4**.

The $^{31}P\{^1H\}$ NMR spectrum of **4** measured in CD_2Cl_2 at room temperature exhibits a singlet at −17.0 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the benzoyl carbonyl carbon and the *O*-ethylated carbamoyl carbon appear as broad triplets at δ 251.6 and 223.9, respectively. In the ^1H NMR spectrum the methylene protons bonded to the α-carbons in the piperidino ring are observed as three broad signals at δ 4.23, 3.97, and 3.66 in 1/1/2 ratio. On raising the temperature to 66 °C, the former two signals coalesce into a broad signal at δ 4.1, while the latter remains as a separate broad peak. As suggested by IR spectroscopy, the C–N bond in the *O*-ethylated carbamoyl group possesses double-bond character that restricts rotation around the C–N bond and makes the two α-CH_2 groups in the piperidino group non-equivalent. Thus, the two broad signals observed at 66 °C are ascribed to the

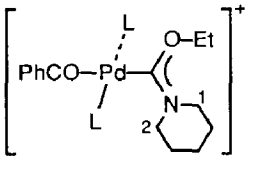
Table 2

IR and NMR data for benzoyl complexes with *O*-ethylated carbamoyl ligands (**4**, **5** and **6**)

Complex	$^{13}C\{^1H\}$ NMR [a]		^1H NMR [b]		$^{31}P\{^1H\}$ NMR [c] (ppm)	IR (cm^{-1}) [d]
	δ	Assignment	δ	Assignment		
4	15.4 (t) [e]	PMe	1.21 (t, 18H) [j]	PMe	−17.0 (s)	1606
	15.5 (s) [s]	OCH_2CH_3	1.5–1.9 (br, 9H)	OCH_2CH_3		(ν(CO))
	23.8 (s) [s]	$NCH_2CH_2CH_2$		and $NCH_2(CH_2)_3$		1529 [q]
	25.7 (s) [t]	NCH_2CH_2	3.66 (br, 2H) [u]	NCH_2		(ν(NCO))
	25.9 (s) [t]	NCH_2CH_2	3.97 (br, 1H) [u]	$NC'H_2$		
	26.9 (s) [s]	$NCH_2C'H_2$	4.23 (br, 1H) [u]	$NC'H_2$		
	45.2 (s) [t]	NCH_2	4.66 (q, 1H) [k,u]	OCH_2		
	44.9 (s) [t]	NCH_2	4.93 (q, 1H) [k,u]	OCH_2		
	53.2 (s) [s]	$NC'H_2$				
	71.2 (s) [t]	OCH_2				
	71.6 (s) [t]	OCH_2				
	223.9 (t) [e]	$C(OEt)(NR_2)$				
	251.6 (t) [e]	PhCO				
5	14.4 (s)	OCH_2CH_3	0.88 (t, 3H) [k]	OCH_2CH_3	13.4 (s) [m]	1604
	36.5 (s)	NMe	2.29 (s, 3H)	NMe		(ν(CO))
	42.7 (s)	NMe′	3.20 (s, 3H)	NMe′		1565 [r]
	70.7 (s)	OCH_2	4.47 (q, 3H) [k]	OCH_2		(ν(NCO))
	219.8 (t) [f]	$C(OEt)(NMe_2)$				
	238.5 (t) [g]	PhCO				
6	14.8 (s)	OCH_2CH_3	1.12 (t, 3H) [k]	OCH_2CH_3	12.1 (d) [n,o]	1613
	37.0 (s)	NMe	2.25 (s, 3H)	NMe	17.1 (d) [n,p]	(ν(CO))
	44.7 (s)	NMe′	3.31 (s, 3H)	NMe′		1565 [r]
	72.0 (s)	OCH_2	4.67 (dq, 1H) [l]	OCH_2		(ν(NCO))
			5.50 (dq, 1H) [l]	$OC'H_2$		
	204.0 (dd) [h]	$C(OEt)(NMe_2)$				
	228.7 (dd) [i]	PhCO				

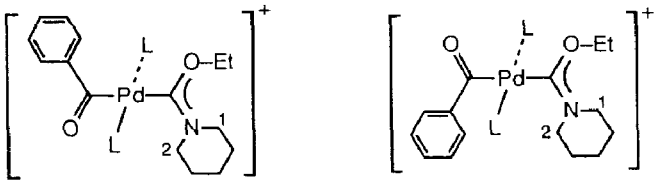
[a] 125 MHz, in $CDCl_3$ (**4**) or 67.8 MHz, in CD_2Cl_2 (**5** and **6**), at room temperature. [b] 270 MHz, in CD_2Cl_2, at room temperature; chemical shifts are relative to an external PPh_3 standard (downfield positive). [c] 40 MHz, in CD_2Cl_2, at room temperature. [d] In KBr disk. [e] The coupling constant is obscure due to broadening. [f] ^2J(P–C) 12 Hz, ^1J(Pt–C) 813 Hz. [g] ^2J(P–C) 7 Hz. [h] ^2J(P–C) 12 and 117 Hz, ^1J(Pt–C) 1291 Hz. [i] ^2J(P–C) 9 and 100 Hz. [j] J(P–H) 3.7 Hz. [k] ^3J(H–H) 7 Hz. [l] ^3J(H–H) 7 Hz, ^2J(H–H) 9 Hz. [m] ^1J(Pt–P) 3020 Hz. [n] ^2J(P–P) 22 Hz. [o] ^1J(Pt–P) 2631 Hz. [p] ^1J(Pt–P) 1422 Hz. [q] ν($N^{13}CO$) 1509 cm^{-1}. [r] ν($N^{13}CO$) 1543 cm^{-1}. [s] For $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$. [t] For $\mathbf{4}_{syn}$ or $\mathbf{4}_{anti}$. [u] See text.

two α-methylene groups C^1H_2 and C^2H_2 in the piperidino ring (eq. 9). The rotation around the C–N bond is expected to occur at much higher temperatures.



(9)

On the other hand, splitting of the signals arising from one of the α-CH_2 groups at room temperature may be attributed to the presence of two rotational isomers anti and syn in a 1/1 ratio.



(10)

4_{anti} (L = PMe_3) 4_{syn}

Thus the biggest signal observed at δ 3.66 is assignable to the α-methylene protons in the piperidino group on the opposite side of the benzoyl group (α-C^1H_2) in the *anti* and *syn* isomers. On the other hand, the resonances at δ 4.23 and 3.97 are assignable to the α-C^2H_2 protons situated closer to the benzoyl group in each isomer. In this case chemical shift of the α-C^2H_2 protons may be different in each isomer, probably due to different influence of ring current of the phenyl group. The presence of the *anti* and *syn* isomers is suggested also by appearance of two sets of quartets arising from the CH_2 protons in the OEt group at δ 4.93 and 4.66 in the ^1H NMR spectrum at room temperature. These two signals coalesce into a broad signal at 66 °C.

X-ray structure of ***4***

The crystal structure of the *syn* isomer of **4** has been determined by means of single X-ray diffraction analysis. Complex **4** has a slightly distorted square planar structure with the benzoyl and *O*-ethylated carbamoyl groups in mutually *trans* positions (Fig. 2) *. The Pd–P lengths (2.316 Å) are normal (Table 3). The distance

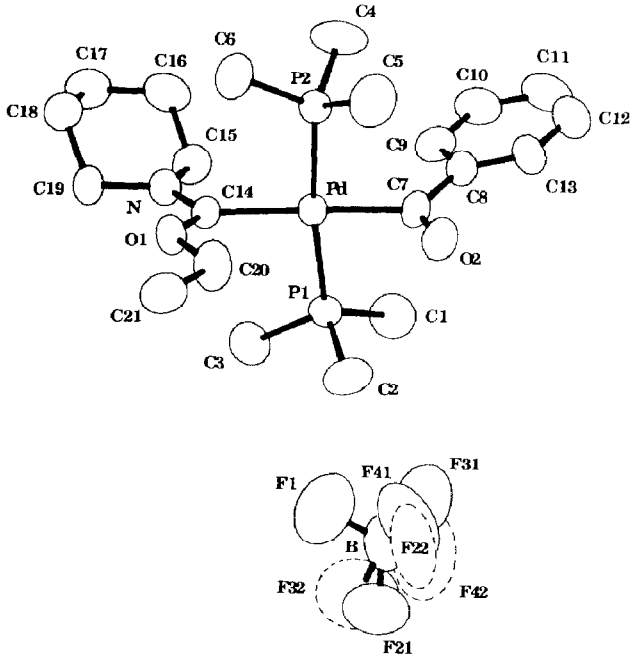


Fig. 2. An ORTEP drawing of *trans*-[Pd(COPh){C(OEt)($\overline{N(CH_2)_4CH_2}$)}(PMe_3)$_2$]BF_4 (**4**).

* The BF_4 anion has two types of orientation approximately in same probability in the crystal (see Experimental).

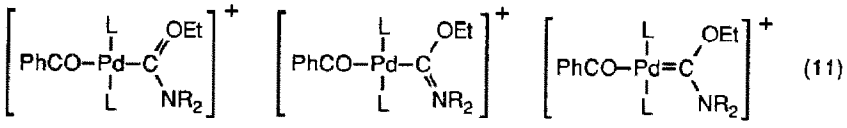
Table 3

Bond distances (Å) and angles (deg) for *trans*-[Pd(COPh){C(OEt)($\overline{N(CH_2)_4CH_2}$)}$(PMe_3)_2$]BF_4 (4)

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd–P1	2.316(2)	Pd–P2	2.316(2)	Pd–C7	2.023(7)
Pd–C14	2.0845(6)	P1–C1	1.828(10)	P1–C2	1.816(7)
P1–C3	1.823(8)	P2–C4	1.806(8)	P2–C5	1.800(9)
P2–C6	1.824(11)	O1–C14	1.329(7)	O1–C20	1.463(9)
O2–C7	1.201(7)	N–C14	1.298(7)	N–C15	1.482(8)
N–C19	1.494(10)	C7–C8	1.493(9)	C8–C9	1.403(10)
C8–C13	1.393(11)	C9–C10	1.401(10)	C10–C11	1.421(20)
C11–C12	1.355(17)	C12–C13	1.379(15)	C15–C16	1.542(11)
C16–C17	1.534(13)	C17–C18	1.506(13)	C18–C19	1.577(10)
C20–C21	1.495(10)	B–F1	1.359(22)	B–F21	1.375(31)
B–F22	1.322(29)	B–F31	1.383(25)	B–F32	1.255(36)
B–F41	1.255(43)	B–F42	1.263(37)		
Atoms	**Angle**	**Atoms**	**Angle**	**Atoms**	**Angle**
C7–Pd–C14	172.1(2)	C7–Pd–P1	86.6(2)	C7–Pd–P2	86.2(2)
C14–Pd–P1	96.0(2)	C14–Pd–P2	91.4(2)	P1–Pd–P2	172.6(1)
C2–P1–C3	102.8(4)	C2–P1–C1	103.7(4)	C2–P1–Pd	111.1(3)
C1–P1–C3	103.7(5)	C1–P1–Pd	117.3(3)	C3–P1–Pd	116.7(4)
C4–P2–C5	104.3(5)	C5–P2–C6	103.5(5)	Pd–P2–C5	115.2(4)
C4–P2–C6	101.0(4)	C4–P2–Pd	114.1(4)	C6–P2–Pd	117.0(3)
C14–O1–C20	116.2(5)	C14–N–C15	120.9(6)	C14–N–C19	124.0(5)
C15–N–C19	115.0(5)	O2–C7–C8	119.5(6)	O2–C7–Pd	118.3(5)
Pd–C7–C8	122.1(4)	C9–C8–C13	120.2(7)	C7–C8–C13	120.0(6)
C9–C8–C7	119.8(6)	C8–C9–C10	120.3(8)	C9–C10–C11	117.1(8)
C12–C8–C10	122.3(10)	C11–C12–C13	120.3(11)	C8–C13–C12	119.9(8)
N–C14–O1	111.8(5)	N–C14–Pd	125.4(4)	O1–C14–Pd	122.6(4)
N–C15–C16	110.5(7)	C15–C16–C17	110.3(6)	C16–C17–C18	110.5(6)
C17–C18–C19	111.4(8)	N–C19–C18	108.5(5)	O1–C20–C21	107.1(7)
F41–B–F21	102.6(24)	F41–B–F1	98.7(26)	F21–B–F1	116.3(17)
F41–B–F31	98.9(22)	F21–B–F31	133.8(23)	F31–B–F1	99.9(16)
F42–B–F22	118.2(27)	F42–B–F32	81.2(34)	F32–B–F22	111.8(26)
F42–B–F1	124.4(19)	F22–B–F1	115.5(23)	F32–B–F1	92.2(22)

between the carbonyl carbon (C7) and the palladium center is 2.023 Å which is somewhat shorter than the sum of the covalent radii of Pd^{II} and sp^2 carbon (2.05 Å), indicating a slight π-bonding character of the Pd–COPh bond. In contrast, the *O*-ethylated carbamoyl-palladium distance (Pd–C14 2.084 Å) is typical of a Pd–C single bond. In the *O*-ethylated carbamoyl ligand, the distance between the Pd-bound carbon (C14) and the nitrogen (1.298 Å) is significantly shorter than that for a typical C–N single bond. The C14–O1 bond length (1.329 Å) is longer than the C7–O2 bond in the benzoyl group (1.201 Å) but still shorter than a C–O single bond (ca. 1.5 Å). The Pd, C14, O1, N, C15, C19, and C20 atoms are approximately in a plane, reflecting delocalization of π electrons over the C–N and C–O bonds in the *O*-ethylated carbamoyl ligand.

Complex **4** has three limiting description of bonding.



(11)

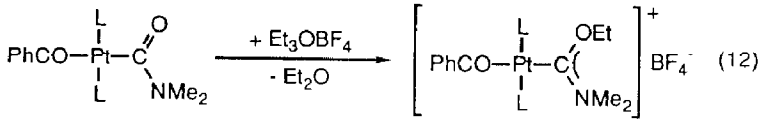
The X-ray structure indicates predominant contributions of **X** and **Y**, and a negligible contribution of **Z** with a Pd–C double bond. Thus, although complex **4** is assumed formally as an ethoxyaminocarbene complex, the ethoxyaminocarbene ligand has little carbene character but should be regarded as an *O*-ethylated carbamoyl ligand which is bound to palladium by a single bond.

Preparation of trans- and cis-[Pt(COPh){(C(OEt)(NMe$_2$)}(PPh$_3$)$_2$]BF$_4$ (5 and 6)

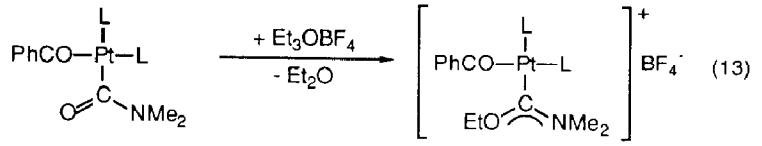
Cationic benzoyl complexes with *O*-ethylated carbamoyl ligands can be prepared also with platinum analogs. Reactions of *trans*- and *cis*-Pt(COPh)(CONMe$_2$)(PPh$_3$)$_2$ with Et_3OBF_4 in CH_2Cl_2 afford the title compounds **5** and **6**, respectively, with retention of the original geometries at the platinum centers.

The spectroscopic data of **5** and **6** are listed in Table 2. The $^{13}C\{^1H\}$ NMR spectrum of the *trans* complex **5** exhibits two sets of triplets with ^{195}Pt satellites at δ 219.8 (J(P–C) 12 Hz) and 238.5 (J(P–C) 7 Hz) assignable to the *O*-ethylated carbamoyl carbon and the benzoyl carbon, respectively. The triplet at δ 219.8 markedly increases in intensity in the spectrum of ^{13}C-labeled *trans*-[Pt(COPh)-{^{13}C(OEt)(NMe$_2$)}(PPh$_3$)$_2$]BF$_4$ (**5**-^{13}C). The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a singlet with ^{195}Pt satellites at 13.4 ppm (^1J(Pt–P) 3020 Hz). In the ^1H NMR spectrum the two N–Me groups appear as non-equivalent two-singlet peaks at δ 2.29 and 3.20 owing to restricted rotation around the *O*-ethylated carbamoyl carbon–nitrogen bond. The IR spectrum of **5** shows two strong absorptions at 1604 and 1565 cm^{-1}. The latter absorption shifts to 1543 cm^{-1} in the ^{13}C-labeled complex **5**-^{13}C. The frequency is in fair agreement with the calculated value for ν(O–^{13}C–N) band (1542 cm^{-1}).

The benzoyl carbon and the *O*-ethylated carbamoyl carbon in the *cis* isomer **6** are observed as two sets of doublet of doublets at δ 228.7 (J(P–C) 9 and 100 Hz) and 204.0 (J(P–C) 12 and 117 Hz), respectively, in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **6** exhibits an AB quartet signal with ^{195}Pt satellites. The two N–Me groups are observed as two sets of singlets at δ 2.35 and 3.31 in the ^1H NMR spectrum. The IR spectrum shows two strong absorptions at 1613 (for the benzoyl group) and 1565 cm^{-1} (for the *O*-ethylated carbamoyl ligand).



(L = PPh_3) **5**



(L = PPh_3) **6**

Conclusion

In this study an *O*-protonated carbamoylpalladium complex has been found as an intermediate in the nucleophilic attack of secondary amine on a CO ligand to give a carbamoylpalladium complex. Indirect support of the *O*-protonated carbamoyl structure has been obtained by studying related *O*-ethylated carbamoyl-palladium and -platinum complexes. Attachment of the proton to the carbonyl oxygen atom appears to increase the electron-delocalization over the O–C–N bonds providing additional stability to the *O*-protonated carbamoyl structure.

Experimental

All manipulations were carried out under an atmosphere of argon or nitrogen or in vacuo. ^{1}H, ^{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 of our laboratory. ^{1}H and ^{13}C NMR signals were referred to Me_4Si as an internal standard and ^{31}P NMR signals to PPh_3 as an external reference. IR spectra were recorded on a JASCO IR-810 spectrometer. Elemental analyses were carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory by using a Yanagimoto CHN autocorder type MT-2. Solvents and amines were dried in usual manner, distilled, and stored under argon atmosphere. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. ^{13}CO (99% isotopic purity) was purchased from CEA. *trans*-[Pd(COPh)(acetone)$(PMe_3)_2$]BF_4 was prepared by the reaction of *trans*-Pd(COPh)(Cl)$(PMe_3)_2$ with an equimolar amount of $AgBF_4$ in acetone and characterized by means of NMR and IR spectroscopy and elemental analysis [6].

*Preparation of trans-[Pd(COPh)(CO)$(PMe_3)_2$]BF_4 (**1**)*

The complex *trans*-[Pd(COPh)(acetone)$(PMe_3)_2$]BF_4 (0.56 g, 0.11 mmol) was dissolved in CH_2Cl_2 (2 ml) at $-20\,^{\circ}C$. The solvent was then evaporated by bubbling CO gas into the solution at room temperature for 30 min to give an off-white powder of complex **1** (0.52 g, 99%). Since complex **1** is unstable in the solid state as well as in solution in the absence of free CO and it readily releases the CO ligand to give an uncharacterized cationic benzoylpalladium species, analytically pure complex **1** could not be isolated. Under CO, on the other hand, complex **1** is fairly stable in solution and could be characterized by NMR spectroscopy (Table 1).

*NMR examinations on the reaction of trans-[Pd(COPh)(CO)$(PMe_3)_2$]BF_4 (**1**) with pyrrolidine*

*(a) Characterization of trans-[Pd(COPh){C(OH)($\overline{N(CH_2)_3CH_2}$)}$(PMe_3)_2$]BF_4 (**2**).* A CD_2Cl_2 solution (1 ml) of *trans*-[Pd(COPh)(CO)$(PMe_3)_2$]BF_4 was prepared from isolated *trans*-[Pd(COPh)(acetone)$(PMe_30_2]BF_4$ (51 mg, 0.10 mmol) and CO at atmospheric pressure. The system was cooled to $-40\,^{\circ}C$ and pyrrolidine (17 μl, 0.20 mmol) was added. The resulting orange solution was transferred into an NMR sample tube under CO atmosphere and examined by NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum measured at $-50\,^{\circ}C$ exhibited a singlet at -12.0 ppm due to complex **2**. No other signal was detected. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

showed the presence of **2** and free pyrrolidine in a 1/1 ratio. The NMR data of complex **2** are listed in Table 1.

(b) Studies on the equilibrium between trans-[Pd(COPh){C(OH)(N(CH$_2$)$_3$CH$_2$)}-(PMe$_3$)$_2$]BF$_4$ (2) and trans-Pd(COPh)(CON(CH$_2$)$_3$CH$_2$)(PMe$_3$)$_2$ (3). A pale yellow solution of the cationic benzoyl(carbonyl)palladium complex (**1**) in a CH_2Cl_2/CD_2Cl_2 mixture was prepared from *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]BF_4 (71.1 mg, 0.140 mmol), CH_2Cl_2 (1.40 ml), CD_2Cl_2 (0.10ml), and atmospheric pressure of CO. The solution was cooled to −20 °C and pyrrolidine (70 μl, 0.84 mmol) was added. The $^{31}P\{^1H\}$ NMR spectrum of the resulting orange solution measured at −60 °C exhibited two singlets assignable to **2** and **3** in a ratio of 7.0/3.0. Based on the initial concentrations of **1** and pyrrolidine and the relative ratio of **2** and **3** observed in the NMR spectrum, the equilibrium constant between **2** and **3** (K_{eq} = [**3**][CH$_2$(CH$_2$)$_3$NH$_2$BF$_4$]/[**2**][CH$_2$(CH$_2$)$_3$NH]) was estimated to be 0.027. In similar methods the equilibrium constants were measured at four other different concentrations of pyrrolidine ([pyrrolidine] = 0.88, 1.36, 2.31, and 3.75 *M*). The K_{eq} values thus obtained were in fair agreement with each other (0.028 ± 0.002).

A solution of trans-[Pd(COPh)(CO)(PMe_3)$_2$]BF_4 (**1**) in a CD_2Cl_2/CH_2Cl_2 mixture was prepared from *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]BF_4 (28.0 mg, 0.055 mmol), CD_2Cl_2 (0.30 ml), CH_2Cl_2 (0.70 ml), and CO at atmospheric pressure. The solution was cooled to −20 °C and pyrrolidine (100 μl, 1.20 mmol) was added. The $^{31}P\{^1H\}$ NMR spectra (200 MHz) of the resulting solution at six different temperatures are illustrated in Fig. 1. Rate constants (k_{obsd}) for the equilibration between **2** and **3** were determined by a conventional line broadening technique using data from a static spectrum measured at −80 °C: k_{obsd} (s^{-1}) = 4.4 (−50 °C), 10.7 (−40 °C), 28.0 (−30 °C), 69.1 (−20 °C), 161 (−10 °C), 342 (0 °C) [9]. An Arrhenius plot for the rate constants gave a straight line with correlation coefficient of 0.999. The activation parameters are given in the text.

Preparation of trans-Pd(COPh)(CON(CH$_2$)$_3$CH$_2$)(PMe$_3$)$_2$ (3)

Pyrrolidine (0.37 ml, 4.4 mmol) was added at −20 °C to an acetone solution (2 ml) of the cationic benzoyl(carbonyl)palladium complex (**1**) prepared in situ from *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]BF_4 (0.45 g, 0.89 mmol) and CO at atmospheric pressure. The pale yellow solution turned orange instantly. The solution was treated with Et_3N (1 ml), and the system was allowed to stand at −20 °C under a CO atmosphere for 3 days to form red crystals of **3**. The product was filtered, washed with cold acetone and then with ether, and dried under vacuum (0.17 g, 41%). Anal. Found: C, 47.6; H, 7.1; N, 3.1. $C_{18}H_{31}NO_2P_2Pd$ calcd.: C, 46.8; H, 6.8; N, 3.0%. The spectroscopic data are listed in Table 1.

Similarly prepared was *trans*-Pd(COPh)(CON(CH$_2$)$_4$CH$_2$)(PMe_3)$_2$ by using piperidine in place of pyrrolidine (red crystals, 41%). Anal. Found: C, 48.1; H, 7.4; N, 2.9. $C_{19}H_{33}NO_2P_2Pd$ calcd.: C, 48.0; H, 6.9; N, 2.9%. IR (KBr): 1565 (benzoyl C=O), 1528 (carbamoyl C=O) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.13 (t, *J* 3.5 Hz, 18H, P–Me), 1.5 (br, 6H, NCH$_2$(CH$_2$)$_3$), 3.4 (br, 2H, NCH$_2$), 3.8 (br, 2H, NCH$_2'$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −12.0 ppm (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 15.6 (t, *J* 15 Hz, P–Me), 26.4, 26.5 and 27.6 (each singlet, NCH$_2$(CH$_2$)$_3$), 40.5 (s, NCH$_2$), 48.6 (s, NC′H$_2$), 210.4 (t, *J* 13 Hz, CON), 275.0 (t, *J* 10 Hz, PhCO). The ^{13}C-labeled complex *trans*-Pd(COPh)(^{13}CON(CH$_2$)$_4$CH$_2$)(PMe_3)$_2$ was prepared in similar procedure using ^{13}CO in place of CO in natural abundance.

Preparation of trans-[Pd(COPh){C(OEt)(N(CH$_2$)$_4$CH$_2$)}(PMe$_3$)$_2$]BF$_4$ (4)

To a CH_2Cl_2 solution (2 ml) of *trans*-Pd(COPh)(CON(CH$_2$)$_4$CH$_2$)(PMe$_3$)$_2$ (0.29 g, 0.60 mmol), was added Et_3OBF_4 (0.11 g, 0.60 mmol) at $-30\,^\circ$C. The solution was stirred for 20 min at $0\,^\circ$C. The red solution turned yellow. Then Et_2O (15 ml) was slowly added at room temperature to afford a yellow precipitate, which was filtered, washed with Et_2O (2 ml × 2), and dried under vacuum. The crude product was recrystallized from a CH_2Cl_2/Et_2O mixture at $-20\,^\circ$C to give yellow crystals of **4** (0.30 g, 85%). Anal. Found: C, 42.4; H, 6.8; N, 2.3. $C_{21}H_{28}NO_2P_2BF_4Pd$ calcd.: C, 42.6; H, 6.4; N, 2.4%.

X-ray diffraction study of complex 4

Crystal data. $C_{21}H_{38}NO_2P_2PdBF_4$, $M = 591.70$; monoclinic, a 28.449(36), b 10.249 (8), c 19.952 (24), β 110.66 (9); V 5443.5 Å^3; D_c 1.45 g cm^{-3}; $Z = 8$; space group $C2/c$; μ(Mo-K_α) 8.31 cm^{-1}. A yellow crystal of dimensions ca. 0.3 × 0.4 × 0.4 mm was used for data collection.

Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer using monochromated Mo-K_α radiation (λ 0.709260 Å). Unit cell dimensions and an orientation matrix were obtained by a least-squares calculation for 18 automatically centred reflections in the range $20 \leq 2\theta \leq 25\,^\circ$. Diffraction intensities were measured at 19°C in the range $3 \leq 2\theta \leq 50\,^\circ$ using ω–2θ scan technique at a scan rate of 4°/min. Three standard reflections, measured at every 100 reflection measurements, showed no decrease in intensity during data collection. No absorption correction was made. Of the 4823 unique reflections measured, 4125 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 R-CRYSTAN program. The Pd atom was positioned from a Patterson map, and all other non-hydrogen atoms by subsequent Fourier syntheses. Hydrogen atoms were not located. The difference maps suggested two types of orientation for the BF_4 anion approximately in same probability. The structure was refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The final R factor was 0.054 ($R_w = 0.054$). Fractional coordinates and equivalent isotropic thermal parameters are listed in Table 4. Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

Preparation of trans-[Pt(COPh){C(OEt)(NMe$_2$)}(PPh$_3$)$_2$]BF$_4$ (5)

To a CH_2Cl_2 solution (2 ml) of *trans*-Pt(COPh)(CONMe$_2$)(PPh$_3$)$_2$ (0.44 g, 0.49 mmol) [6], was added Et_3OBF_4 (0.092 g, 0.49 mmol) at $-20\,^\circ$C. The color of the solution changed instantly from orange the yellow. After stirring for 1 h, Et_2O (15 ml) was added slowly to the solution to afford yellow crystals of complex **5**, which was filtered, washed with acetone (3 ml × 2), and dried under vacuum (0.33 g, 66%). Anal. Found: C, 56.6; H, 4.9; N, 1.4. $C_{48}H_{46}NO_2P_2PtBF_4$ calcd.: C, 56.9; H, 4.6; N, 1.4%. The spectroscopic data are given in Table 2. The ^{13}C-labeled complex *trans*-[Pt(COPh){^{13}C(OEt)(NMe$_2$)}(PPh$_3$)$_2$]BF$_4$ (**5**-^{13}C) was prepared similarly from *trans*-Pt(COPh)(^{13}CONMe$_2$)(PPh$_3$)$_2$ in place of the non-labeled benzoyl-carbamoyl complex.

Table 4

Fractional coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters for *trans*-[Pd(COPh){C(OEt)(N(CH$_2$)$_4$CH$_2$)}(PMe$_3$)$_2$]BF$_4$ (**4**)

Atom	*x*	*y*	*z*	B_{eq} [a]
Pd	0.15441(2)	0.45736(3)	0.65483(2)	3.15
P1	0.22406(6)	0.37639(15)	0.63410(7)	3.85
P2	0.08548(6)	0.56130(15)	0.66668(9)	3.72
O1	0.1595(2)	0.2805(4)	0.7780(2)	4.04
O2	0.1999(2)	0.7008(4)	0.6586(3)	5.43
N	0.1136(2)	0.1942(5)	0.6765(3)	3.66
C1	0.2302(3)	0.4165(10)	0.5482(4)	6.97
C2	0.2818(3)	0.4387(8)	0.6998(4)	6.07
C3	0.2334(3)	0.2002(7)	0.6414(5)	6.73
C4	0.0327(3)	0.5774(11)	0.5837(4)	7.41
C5	0.0969(4)	0.7245(8)	0.7021(6)	8.01
C6	0.0556(3)	0.4819(9)	0.7231(5)	7.21
C7	0.1696(2)	0.6298(6)	0.6175(3)	4.06
C8	0.1420(2)	0.6748(6)	0.5426(3)	4.63
C9	0.1142(3)	0.5848(8)	0.4909(4)	4.82
C10	0.0877(3)	0.6264(11)	0.4208(4)	7.01
C11	0.0898(4)	0.7624(15)	0.4063(6)	9.34
C12	0.1172(4)	0.8482(11)	0.4564(7)	8.27
C13	0.1431(3)	0.8062(8)	0.5251(5)	6.60
C14	0.1420(2)	0.2919(5)	0.7070(3)	3.28
C15	0.0936(3)	0.1813(6)	0.5974(3)	4.52
C16	0.0363(3)	0.1602(8)	0.5701(4)	5.94
C17	0.0231(3)	0.0425(7)	0.6076(5)	6.15
C18	0.0436(3)	0.0606(7)	0.6876(5)	5.60
C19	0.1021(3)	0.0822(6)	0.7162(4)	4.77
C20	0.1931(3)	0.3844(8)	0.8178(4)	5.75
C21	0.2120(3)	0.3453(8)	0.8950(4)	5.66
B	0.3924(7)	0.2723(14)	0.6054(8)	8.65
F1	0.3592(3)	0.1893(10)	0.6190(4)	13.6
F21	0.4403(13)	0.2329(55)	0.6370(26)	17.7
F31	0.3632(8)	0.3101(25)	0.5377(11)	13.0
F41	0.3867(17)	0.3745(36)	0.6386(22)	16.1
F22	0.4051(14)	0.3738(30)	0.6472(17)	12.3
F32	0.4246(13)	0.1858(25)	0.6180(25)	25.1
F42	0.4004(12)	0.2776(33)	0.5465(11)	18.8

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

*Preparation of cis-[Pt(COPh){C(OEt)(NMe$_2$)}(PPh$_3$)$_2$]BF$_4$ (**6**)*

To a CH_2Cl_2 solution (1 ml) of *cis*-Pt(COPh)(CONMe$_2$)(PPh$_3$)$_2$ (0.20 g, 0.22 mmol) [6], was added Et_3OBF_4 (0.042 g, 0.22 mmol) at −30 °C. After stirring the system for 10 min, Et_2O (10 ml) was added slowly to afford a yellow precipitate of complex **6**, which was filtered, washed with acetone (2 ml × 3), and dried under vacuum (0.17 g, 75%). Anal. Found: C, 56.9; H, 4.9; N, 1.4. $C_{48}H_{46}NO_2P_2PtBF_4$ calcd.: 56.9; H, 4.6; N, 1.4%. The spectroscopic data are given in Table 2. The ^{13}C-labeled complex **6**-^{13}C was prepared by similar procedure using *cis*-Pt(COPh)(^{13}CONMe$_2$)(PPh$_3$)$_2$ as a starting material.

References

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