−50 °C using toluene and pentane gave analytically pure dark green crystals of **3c**. The average yield based on the amount of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(1,5\text{-}COD)$ was 18%. ^1H NMR (CD_2Cl_2, −10 °C) δ 7.58 (d, 1 H, J_{CH} = 7.3 Hz, H_u), 7.13 (t, 1 H, H_{pa}), 6.98 (d, 1 H, J_{CH} = 7.3 Hz, H_d), 6.62 (t, 1 H, H_{md}), 6.36 (d, 1 H, J_{CH} = 7.8 Hz, H_{mu}), 6.02 (m, 5 H, Cp_{down}), 5.89 (d, 1 H, J_{CH} = 6.8 Hz, H_0), 4.84 (m, 5 H, Cp_{up}), 4.17 (m, 1 H, olefinic COD), 3.89 (s, 3 H, OMe), 3.89 (m, 1 H, olefinic COD), 3.46 (m, 1 H, olefinic COD), 2.99 (m, 1 H, olefinic COD), 2.42–2.28 (m, 4 H, COD), 2.06–1.92 (m, 4 H, COD); ^{13}C NMR (CD_2Cl_2, −10 °C) δ 197.8 (dt, J_{CH} = 130, J_{CRh} = 22 Hz, μ-CH_2), 175.1 (d, J_{CRh} = 31.5 Hz, C_i), 171.7 (s, C_{OMe}), 127.8 (d, J_{CH} = 159 Hz, C_{pa}), 126.8 (d, J_{CH} = 156 Hz, C_o), 124.3 (d, J_{CH} = 162 Hz, C_{md}), 104.0 (d, J_{CH} = 157 Hz, C_{mu}), 107.8 (m, J_{CH} = 172 Hz, Cp), 107.2 (m, J_{CH} = 174 Hz, Cp), 88.7 (dd, J_{CH} = 157, J_{CRh} = 8.8 Hz, olefinic COD), 87.6 (dd, J_{CH} = 156, J_{CRh} = 8.1 Hz, olefinic COD), 78.9 (dd, J_{CH} = 149, J_{CRh} = 8.1 Hz, olefinic COD), 31.9 (t, J_{CH} = 128 Hz, COD), 29.9 (t, J_{CH} = 125 Hz, COD), 29.4 (t, J_{CH} = 130 Hz, COD), 28.9 (t, J_{CH} = 127 Hz, COD). Anal. Calcd for $C_{26}H_{31}OTiRh$: C, 61.19; H, 6.12. Found: C, 61.35; H, 6.03.

Crystal Structure Determination of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}p\text{-}Me_2NC_6H_4)Rh(1,5\text{-}COD)$. A dark green acicular crystal of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}p\text{-}Me_2NC_6H_4)Rh(1,5\text{-}COD)$ was mounted in a thin-walled glass capillary under nitrogen. Table II lists the data collection parameters. The rhodium atom was found from a Patterson map; the coordinates of the other non-hydrogen atoms were obtained by successive structure factor–Fourier calculations. Hydrogen atoms were initially placed by computation or difference maps and subsequently refined.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference (*International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, pp 71, 149). $R = \sum|F_o - F_c|/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned based on counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. No absorption or secondary extinction corrections were required.

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Supplementary Material Available: Tables listing final parameters, complete distances, complete angles, and anisotropic displacement parameters (6 pages); a table of structure factors (16 pages). Ordering information is given on any current masthead page.

First Structurally Characterized Cis Acyl Carbamoyl Complexes of Platinum(II). Model Study of Palladium-Catalyzed Double-Carbonylation Reactions

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Neutral acyl carbamoyl complexes of platinum(II), *cis*-$Pt(COPh)(CONR_2)(PPh_3)_2$ (R = Me (**3a**), Et (**3b**)), were prepared by nucleophilic attack of $LiNMe_2$ and Et_2NH, respectively, at the CO ligand of *cis*-$[Pt(COPh)(CO)(PPh_3)_2](BF_4)$ (**2**), generated in situ by Ag^+-induced CO deinsertion from *trans*-$Pt(COCOPh)(Cl)(PPh_3)_2$ (**1**). NMR data show that four methylene hydrogens in the carbamoyl ligand of **3b** are diastereotopic. The single-crystal structure of complex **3b**, determined by X-ray diffraction, is a distorted square plane with ∠C1–Pt–C6 = 79.6 (5)°. Such a peculiar small angle causes the distinguishing close distance (only 2.63 (2) Å) between the two carbonyl carbon atoms C1 and C6, which presumably facilitates reductive elimination of the acyl and carbamoyl ligands to yield the double-carbonylated α-keto amide.

Introduction

Acyl carbamoyl complexes, $RC(O)\text{–}M\text{–}C(O)NR'_2$, have been proposed as key intermediates in palladium-catalyzed double-carbonylation reactions, which lead to the formation of α-keto amides.[1] Previous mechanistic studies suggested that acyl carbamoyl species could be formed via a nucleophilic attack at a coordinated CO ligand of an acyl carbonyl complex, $RC(O)\text{–}M\text{–}C(O)$, either by an amine or by an amide.[2] The acyl and carbamoyl groups, if in a cis arrangement, would then facilitate the subsequent reductive elimination to give the double-carbonylated products[3] (Scheme I). However, only a very small number of acyl carbamoyl complexes of Pd(II) and their analogues of Pt(II) have been reported.[4] An acyl alkoxycarbonyl derivative of Pt(II) has been synthesized by nucleophilic

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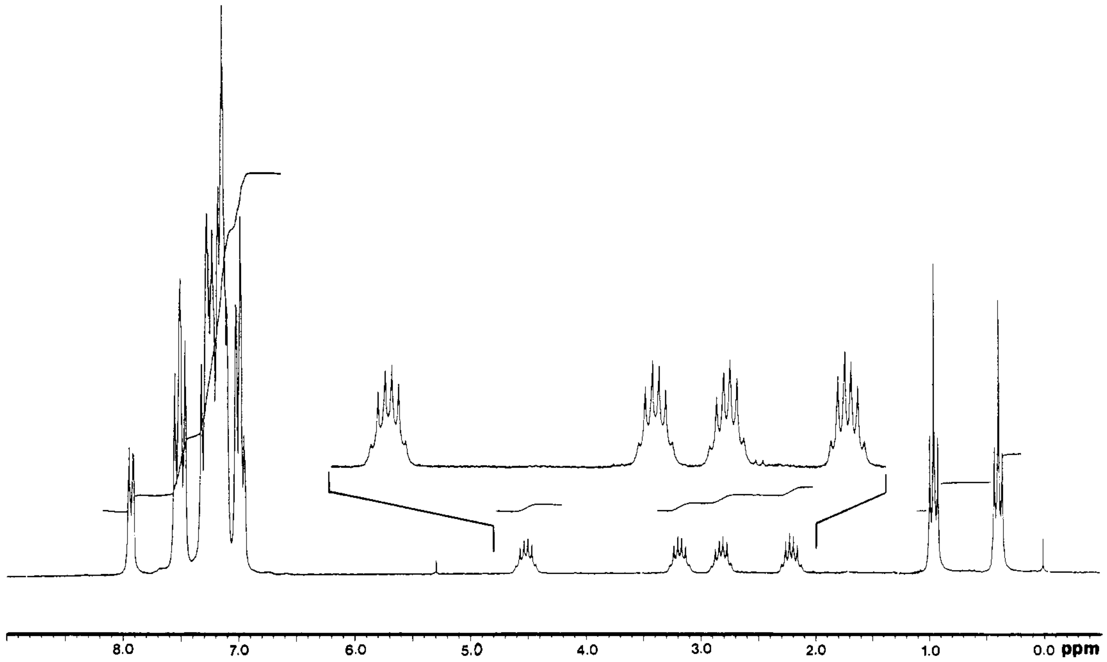
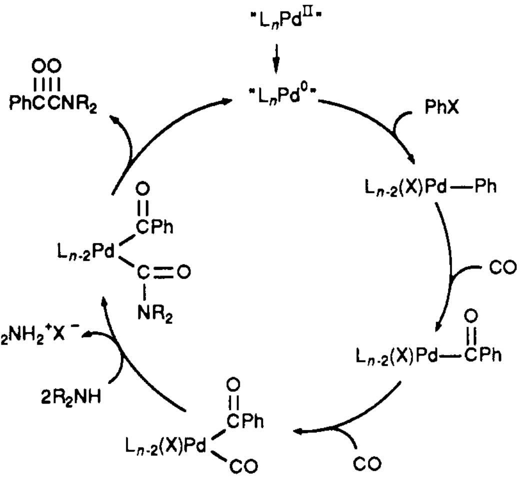
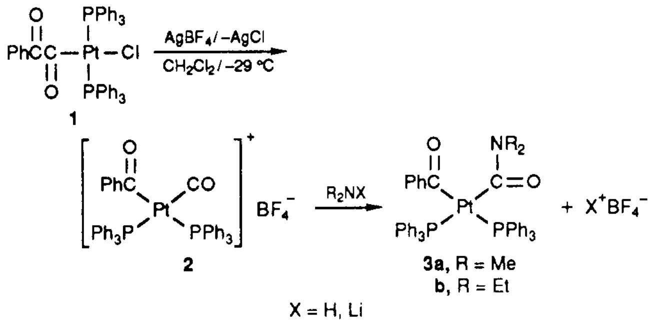


Figure 1. ^1H NMR spectrum of *cis*-Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$.

Scheme I



Scheme II



attack of alkoxide at a cationic (acyl)carbonylplatinum(II) complex.[5] By employing an analogous synthetic strategy, we have prepared the first structurally characterized cis neutral acyl carbamoyl complex of Pt(II). The formation of such a complex and its reductive elimination to yield an α-keto amide make a good model for the palladium-catalyzed double-carbonylation reactions.

Results and Discussion

Synthesis. The abstraction of chloride ion from the benzoylformyl complex *trans*-Pt(COCOPh)(Cl)(PPh$_3$)$_2$ (**1**) by AgBF$_4$ at −29 °C in dichloromethane resulted in the decarbonylation of **1**, yielding *cis*-[Pt(COPh)(CO)(PPh$_3$)$_2$](BF$_4$) (**2**;[5,6] isolated in 90% yield from CH$_2$Cl$_2$/Et$_2$O). Complex **2** underwent a facile isomerization to the stable trans form at 0 °C. The addition of LiNMe$_2$ or Et$_2$NH to the solution of complex **2**, which was preferably prepared in situ to avoid its isomerization, resulted in an instantaneous formation of benzoyl carbamoyl complexes **3a,b** (Scheme II), in isolated yields of 44% and 41%, respectively.

Spectroscopic Characterization of 3a and 3b. In the IR spectra of both **3a** and **3b**, two strong carbonyl absorptions were observed: 1600- and 1542-cm^{-1} bands for **3a** and 1599- and 1545-cm^{-1} bands for **3b**. The lower frequency peaks are assigned to the carbamoyl C=O stretchings according to the data for other carbamoyl ligands.[4]

In the ^{31}P NMR spectrum of **3a** in CDCl$_3$, the two phosphorus resonances accidentally overlap at δ 14.42; however, the P–Pt coupling constants of the two phosphorus atoms, being 1895 and 1577 Hz, are clearly distinguishable. The spectrum of complex **3b** in CDCl$_3$ consists of a pair of doublets at δ 13.77 (J_{P1-Pt} = 1858 Hz) and δ 14.44 (J_{P2-Pt} = 1588 Hz). The chemical and magnetic inequivalence of the two phosphines in each complex indicates that both **3a** and **3b** have a cis square-planar geometry. The J_{P-Pt} values of the phosphorus atoms in such complexes are so sensitive to their corresponding trans ligands that they may serve as criteria for the spectral assignments. According to our previous studies on *cis*-diacyl complexes of Pt(II), the PPh$_3$ ligands trans to the benzoyl ligand usually show their J_{P-Pt} values around 1500–1600 Hz.[5,6] The high-field peaks are therefore assigned to the PPh$_3$ trans to the carbamoyl group, and its P–Pt coupling constants are identified as 1800–1900 Hz.

In the ^1H NMR spectrum of **3a**, the two carbamoyl methyl groups appear well separated at δ 1.97 and 3.16 as

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Table I. X-ray Crystal Parameters and Data Collection for ***cis*-Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$**

formula	$C_{48}H_{45}O_2NP_2Pt$
fw	924.92
space group	*C*2/*c* (No. 15)
a, Å	21.075 (4)
b, Å	9.768 (1)
c, Å	40.546 (8)
β, deg	92.15 (2)
V, Å^3	8341.34
Z	8
ρ(calcd), g cm^{-3}	1.473
radiation (Cu K*α*), λ, Å	1.5418
T, K	300
μ, mm^{-1}	7.38
transmission	0.4877–0.9972
2*θ*, deg	2-120
hkl	$-23 \le h \le 23$, $0 \le k \le 10$, $0 \le l \le 45$
no. of rflns measd	6164
no. of rflns obsd	4986 (>2.0*σ*)
R(*F*)	0.060
R$_w$(*F*)	0.066
S	2.309

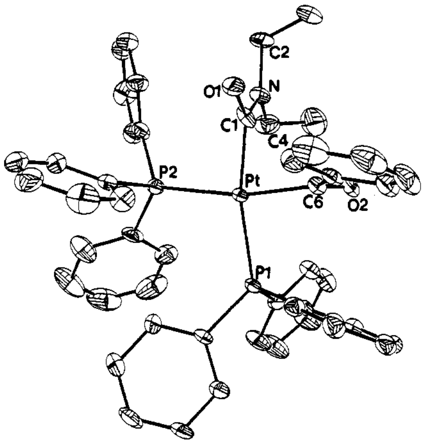


Figure 2. ORTEP drawing of *cis*-Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$.

Table II. Atomic Coordinates for ***cis*-Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$**

	x	*y*	*z*	B_{iso}, Å$^{2\,a}$
Pt	0.194342 (22)	0.13270 (6)	0.128498 (12)	2.491 (19)
P1	0.12210 (13)	0.1467 (3)	0.08304 (7)	2.54 (12)
P2	0.12887 (14)	0.1101 (4)	0.17383 (7)	2.89 (13)
C1	0.2703 (5)	0.1370 (12)	0.1604 (4)	3.1 (6)
C2	0.3439 (8)	0.2646 (24)	0.1979 (4)	7.1 (10)
C3	0.4083 (9)	0.260 (3)	0.1836 (5)	10.3 (16)
C4	0.2575 (8)	0.3911 (19)	0.1668 (4)	5.8 (8)
C5	0.2937 (11)	0.4952 (25)	0.1505 (6)	8.6 (13)
C6	0.2679 (6)	0.1486 (14)	0.0956 (3)	3.1 (6)
C11	0.3001 (6)	0.0229 (15)	0.0842 (3)	3.3 (6)
C12	0.2952 (7)	−0.1011 (17)	0.1004 (4)	5.0 (8)
C13	0.3269 (9)	−0.2137 (19)	0.0887 (5)	6.8 (10)
C14	0.3615 (8)	−0.2039 (22)	0.0607 (5)	7.0 (10)
C15	0.3648 (8)	−0.0807 (22)	0.0438 (5)	6.7 (10)
C16	0.3363 (7)	0.0328 (18)	0.0564 (4)	4.7 (7)
C21	0.0458 (5)	0.0555 (13)	0.0791 (3)	2.9 (5)
C22	0.0222 (7)	−0.0145 (19)	0.1044 (3)	4.8 (8)
C23	−0.0345 (8)	−0.0882 (22)	0.0999 (4)	6.4 (10)
C24	−0.0660 (6)	−0.0905 (19)	0.0698 (4)	5.2 (8)
C25	−0.0437 (6)	−0.0190 (20)	0.0442 (4)	4.9 (8)
C26	0.0133 (6)	0.0543 (19)	0.0482 (4)	4.6 (8)
C31	0.1571 (5)	0.0859 (14)	0.0450 (3)	2.8 (5)
C32	0.1680 (6)	−0.0549 (14)	0.0433 (3)	3.4 (6)
C33	0.1923 (7)	−0.1112 (17)	0.0157 (4)	4.3 (7)
C34	0.2082 (6)	−0.0301 (18)	−0.0104 (3)	4.2 (7)
C35	0.1985 (6)	0.1092 (17)	−0.0090 (3)	3.9 (7)
C36	0.1728 (6)	0.1663 (15)	0.0187 (3)	3.3 (6)
C41	0.1039 (6)	0.3276 (14)	0.0747 (3)	3.2 (6)
C42	0.0422 (6)	0.3765 (17)	0.0687 (4)	5.0 (8)
C43	0.0313 (8)	0.5129 (20)	0.0646 (6)	7.0 (11)
C44	0.0795 (8)	0.6059 (19)	0.0655 (5)	6.7 (10)
C45	0.1414 (7)	0.5606 (17)	0.0718 (4)	5.1 (8)
C46	0.1533 (6)	0.4214 (15)	0.0775 (4)	3.8 (7)
C51	0.0503 (6)	0.1868 (18)	0.1706 (3)	4.2 (7)
C52	0.0447 (7)	0.3102 (19)	0.1533 (4)	5.1 (8)
C53	−0.0136 (10)	0.380 (3)	0.1510 (5)	8.4 (12)
C54	−0.0644 (9)	0.323 (3)	0.1669 (6)	8.5 (12)
C55	−0.0600 (8)	0.202 (3)	0.1837 (6)	8.8 (14)
C56	−0.0023 (8)	0.1353 (21)	0.1857 (5)	6.6 (10)
C61	0.1164 (6)	−0.0711 (16)	0.1836 (3)	3.5 (6)
C62	0.0940 (7)	−0.1153 (18)	0.2136 (4)	4.7 (7)
C63	0.0827 (9)	−0.2540 (21)	0.2195 (4)	6.1 (9)
C64	0.0941 (10)	−0.3432 (20)	0.1955 (5)	7.2 (10)
C65	0.1181 (10)	−0.3056 (19)	0.1658 (5)	6.9 (10)
C66	0.1293 (8)	−0.1678 (16)	0.1600 (4)	4.8 (8)
C71	0.1581 (6)	0.1784 (15)	0.2136 (3)	3.6 (6)
C72	0.2080 (6)	0.1095 (17)	0.2306 (3)	4.1 (7)
C73	0.2322 (7)	0.1618 (19)	0.2607 (4)	5.0 (7)
C74	0.2082 (9)	0.2783 (20)	0.2735 (4)	5.7 (8)
C75	0.1597 (9)	0.3445 (19)	0.2575 (4)	5.9 (9)
C76	0.1347 (8)	0.2938 (17)	0.2280 (4)	4.9 (8)
O1	0.2970 (4)	0.0335 (13)	0.17113 (25)	5.1 (5)
O2	0.2844 (4)	0.2605 (10)	0.08573 (23)	3.8 (4)
N	0.2903 (6)	0.2637 (15)	0.1735 (3)	5.0 (6)

[a] $B_{iso} = (8\pi^2/3)\sum_i\sum_j u_{ij}\, a_i^* a_j^* a_i a_j$.

singlets. An interesting feature in the ^{1}H NMR spectrum of **3b**, as shown in Figure 1, is that all four methylene hydrogens on the carbamoyl ligand are diastereotopic protons, resonating at δ 2.21, 2.82, 3.18, and 4.52 with each being sextets. Decoupling experiments indicate that the first two signals are due to a pair of geminal hydrogens with a coupling constant of 14.0 Hz. These two high-field resonances also coupled with the methyl protons at δ 0.39 with *J* = 7.0 Hz. Similar couplings between the two downfield methylene resonances and the downfield methyl peaks at δ 0.96 were also observed. The diastereotopic protons may likely be due to hindered rotations of the carbamoyl group in **3b** (vide infra).

X-ray Single-Crystal Structure of 3b. Single crystals suitable for X-ray diffraction were grown from CH_2Cl_2/Et_2O cosolvent. Diffraction data were measured on a CAD-4 diffractometer with graphite-monochromated Cu K*α* radiation at 300 K. It was found that **3b** crystallized in space group *C*2/*c*, with *a* = 21.075 (4) Å, *b* = 9.768 (1) Å, *c* = 40.546 (8) Å, *β* = 92.15 (2)°, *V* = 8341.34 Å^3, and *Z* = 8. These and other crystal data are collected in Table I.

The ORTEP drawing of **3b** in Figure 2 confirms that the four ligands around the Pt(II) metal are disposed in a severely distorted square-planar geometry. The benzoyl group and the carbamoyl group of **3b** are in a cis arrangement with ∠C1–Pt–C6 = 79.6 (5)°, which is surprisingly small for two monodentate hydrocarbyl ligands in square-planar Pt(II) complexes, and ∠P1–Pt–P2 = 103.7 (1)°. To our knowledge, the only example that is similar to this one is a *cis*-dibenzoyl analogue.[6] The two carbonyl groups are in the s-trans orientation, with the torsional angle of O1–C1–C6–O2 being 56.02°. Both of the benzoyl and the carbamoyl carbonyls fall in planes that are nearly perpendicular to the molecular plane. The dihedral angle between the P1–P2–C1–C6 plane and the O1–C1–N plane is 89.2 (5)° and is 82.9 (4)° between the P1–P2–C1–C6 plane and the O2–C6–C11 plane. The atomic coordinates and selected bond distances and bond angles for **3b** are listed in Tables II and III, respectively.

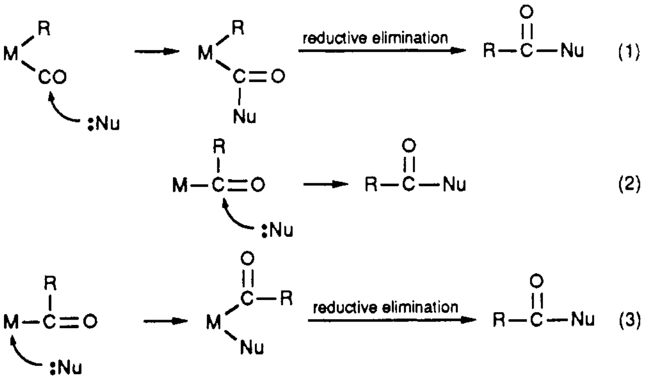
In comparison with the structure of cationic *trans*-[Pd(COPh){C(OEt)(N(CH$_2$)$_4$CH$_2$)}(PMe$_3$)$_2$]BF$_4$, reported previously by Yamamoto et al.,[4d] complex **3b** contains a normal neutral amide that has the bond distances *D*(C1–O1) = 1.23 (2) Å and *D*(C1–N) = 1.41 (2) Å. Recalling the unusual diastereotopic protons observed in the ^{1}H NMR spectrum of **3b**, the magnetic inequivalence of all four

Table III. Selected Bond Distances (Å) and Angles (deg) for *cis*-Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$

Pt-P1	2.350 (3)	C4-N	1.44 (2)	C14-C15	1.39 (3)
Pt-P2	2.350 (3)	C2-C3	1.50 (3)	C15-C16	1.37 (3)
Pt-C1	2.02 (1)	C4-C5	1.45 (3)	P1-C21	1.84 (1)
Pt-C6	2.09 (1)	C6-C11	1.49 (2)	P1-C31	1.83 (1)
C1-O1	1.23 (2)	C11-C16	1.39 (2)	P1-C41	1.84 (1)
C6-O2	1.22 (2)	C11-C12	1.38 (2)	P2-C51	1.82 (1)
C1-N	1.41 (2)	C12-C13	1.38 (2)	P2-C61	1.83 (2)
C2-N	1.47 (2)	C13-C14	1.38 (3)	P2-C71	1.83 (1)
C1-Pt-C6	79.6 (5)	C3-C2-N	115.1 (2)	C12-C11-C16	120.0 (1)
P1-Pt-P2	103.7 (1)	C1-N-C2	118.1 (2)	C11-C12-C13	119.3 (2)
P1-Pt-C1	167.2 (4)	C1-N-C4	123.6 (1)	C12-C13-C14	120.4 (2)
P1-Pt-C6	88.2 (3)	C2-N-C4	118.1 (2)	C13-C14-C15	120.5 (2)
P2-Pt-C1	88.6 (4)	C5-C4-N	115.9 (2)	C14-C15-C16	119.0 (2)
P2-Pt-C6	168.1 (3)	Pt-C6-C11	119.8 (9)	C11-C16-C15	120.6 (2)
Pt-C1-O1	123.4 (1)	Pt-C6-O2	120.3 (1)	C6-C11-C12	122.2 (1)
Pt-C1-N	118.6 (8)	C11-C6-O2	120.0 (1)	C6-C11-C16	117.8 (1)
O1-C1-N	117.7 (1)				

carbamoyl methylene hydrogens is presumably due to hindered rotatations.[12] The hindrance may be attributed to the crowding between the carbamoyl and the benzoyl groups, caused by the exceptionally small angle of ∠C1-Pt-C6, in addition to the amide-inherited restriction of the rotation of the C1-N bond.

Formation of the Carbamoyl Group. Although the high-frequency infrared absorption of the coordinated CO in complex 2 indicates that its carbon atom should be suitable for nucleophilic attack (eq 1),[2a,5] it is worth noting that the acyl carbonyl and the Pt(II) metal center are considered to be eligible for nucleophilic attack as well (eqs 2 and 3). Nucleophilic attack at the metal acyl carbonyl has long been known to be responsible for the formation of carbonylated organic products.[7] However, evidence for such a reaction route, leading to recognizable organometallic species, has only been found for some metal formyls.[8] On the other hand, direct nucleophilic attacks at Pt(II) centers have been well documented.[9] In order to further understand the formation of the carbamoyl group, we monitored the reaction course of the formation of complex **3b** at −30 °C by NMR spectroscopy. Upon the addition of 2 equiv of Et$_2$NH to a solution of complex **2**, the $J_{\mathrm{P-Pt}}$ values of 3740 and 1502 Hz for **2** in its ^{31}P NMR spectrum changed to 1949 and 1566 Hz for **3b** (within 1 min when the first spectrum was accumulated). At the same time, the characteristic ethyl resonances of **3b** (vide supra) appeared in the ^{1}H NMR spectrum. These results provided the proof for the conversion of a CO ligand to a carbamoyl ligand. The rapid and complete transformation from **2** to **3b** as well as the absence of organic amide indicates that the reaction likely involves a nucleophilic attack by Et$_2$NH directly at the CO ligand to yield **3b** as the primary product, although an alternative route such as eq 3 cannot be completely excluded. It appears that the CO ligands, specifically in cationic Pd(II) and Pt(II) complexes, favor nucleophilic attack by hard bases such as alkoxides and amines (or amides).[4,5]



In a general sense, the reactivity of the carbonyl ligand toward nucleophiles could be important to the transition-metal-catalyzed carbonylation reactions. For instance, in the Pd(II)-catalyzed reactions of RX with amine (or alcohol) in the presence of CO, the carbamoyl (or alkoxycarbonyl) groups could exist as the prevailing ligand moieties; therefore, the carbonylated organic products would be likely formed by the reductive elimination of R and −C(O)Nu (eq 1) rather than by external nucleophilic attack on −C(O)R (eq 2). Of course, the formation of RC(O)Nu by the reductive elimination of −C(O)R and −Nu ligands is also a possible route, especially when the CO insertion of R is facile (eq 3).[10] When the acyl group is aroyl, which is inert to CO deinsertion, the reductive elimination of RC(O)− and −C(O)Nu will occur, and the selectivity for double carbonylation will be enhanced. Indeed, the catalytic double-carbonylation reactions likely occur for aryl halides but not alkyl halides.[1e]

Coupling of Acyl and Carbamoyl Groups. The decomposition of complex **3b** in CDCl$_3$ was found to give *trans*-Pt(COPh)(Cl)(PPh$_3$)$_2$ (79%) as the major organometallic product along with PPh$_3$, OPPh$_3$, and some unidentified residues (9% in total). In addition, Et$_2$NH (74%) and PhCOCONEt$_2$ (17%) were identified by ^{1}H NMR spectroscopy by comparison with authentic samples. The formation of PhCONEt$_2$ was not observed. The nearly identical yields of *trans*-Pt(COPh)(Cl)(PPh$_3$)$_2$ and Et$_2$NH (within experimental error) suggest that they may be formed together by the reaction of **3b** with hydrogen chloride, presumably resulting from decomposed solvent. The most intriguing feature is the substantial formation of PhCOCONEt$_2$, the product from the reductive elimination of **3b**. This result is in sharp contrast to that of the analogous reaction of *cis*-Pt(COPh)(COOMe)(PPh$_3$)$_2$,

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in which only <1% of the double-carbonylated ester PhCOCOOMe was observed.[11]

The bond lengths of two Pt–C bonds in the complex **3b** and in the cis benzoyl methoxycarbonyl derivative are similar;[5] therefore, an electronic effect is less likely the cause of the discrepancy in reactivity. A noticeable feature in complex **3b** is the distinguishing close distance (only 2.63 (2) Å) between the two acyl carbons C1 and C6. This distance is significantly shorter than that in *cis*-Pt(COPh)(COOMe)$(PPh_3)_2$, calculated to be 4.008 (4) Å. This is presumably due to the peculiar small ∠C1–Pt–C6 angle. The ground-state steric effect is supposed to be crucial to the feasibility of the reductive elimination in **3b**. This is also consistent with the outcome of palladium(II)-catalyzed double-carbonylation reactions, in which secondary amines are generally better nucleophiles than alcohols. Besides, the steric effect (either of nucleophilic substrates or of phosphines on the catalysts) is generally more critical to the selectivity of double-carbonylated products than is the electronic effect.[1d,e]

Conclusions

The formation of acyl carbamoyl complexes of Pt(II) with the formula *cis*-Pt(COPh)$(CONR_2)(PPh_3)_2$ by nucleophilic attack of amine at the carbonyl ligand of *cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4), as well as the reductive elimination of such acyl carbamoyl complexes leading to the production of α-keto amide, has been shown to be an excellent model for palladium-catalyzed double carbonylation. The structural analysis for *cis*-Pt(COPh)$(CONEt_2)(PPh_3)_2$ indicated that its sterically bulky carbamoyl group and the benzoyl group favor a rotation-hindered s-trans configuration, and the closeness of these two ligands facilitates the subsequent reductive elimination.

Experimental Section

The starting α-keto acyl complex *trans*-Pt(COCOPh)(Cl)$(PPh_3)_2$ (**1**) was prepared according to the literature method.[5] Other reagents were purchased and used without purification. Solvents were dried with use of standard procedures. The IR spectra were recorded on a Perkin-Elmer Model 983G spectrophotometer. The NMR spectra were run on either a Bruker AC-E200 or a Bruker AM-300WB spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency 81.015 MHz was employed, and the chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in $CDCl_3$. Values upfield of the standard are defined as negative.

***cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) (2).** To 200 mg of complex **1** was added 1.2 equiv of $AgBF_4$ (52 mg), followed by 5 mL of degassed CH_2Cl_2 at −29 °C (nitromethane bath). After the removal of AgCl precipitates by filtration, the reaction solution was immediately transfered into 25 mL of cold *n*-hexane to give 210 mg (90%) of **2**. The yellow solids were collected and recrystallized from CH_2Cl_2/Et_2O. IR (KBr): ν_{CO} = 2105, 1635 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 14.36 (3740, 29.2 Hz), 9.19 (1502, 29.2 Hz).

***cis*-Pt(COPh)$(CONMe_2)(PPh_3)_2$ (3a).** Complex **2** was first prepared in situ as above. After the removal of AgCl by filtration, the addition of $LiNME_2$ (an equal molar amount as a suspension in Et_2O) was introduced without prior isolation of **2**, resulting in a dark yellow solution. Additional Et_2O was then introduced to precipitate $LiBF_4$. Yellow crystalline **3a** was obtained in 44% yield by repeated recrystallization from $CH_2Cl_2/Et_2O/n$-hexane. IR (KBr): ν_{CO} = 1600, 1542 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 14.42 (1895, 1576, 19.0 Hz) ^1H NMR ($CDCl_3$): δ 3.16 (s, NCH_3), 1.97 (s, NCH_3).

***cis*-Pt(COPh)$(CONEt_2)(PPh_3)_2$ (3b).** The procedure for the preparation of complex **3b** was the same as that for **3a**, except 2 equiv of Et_2NH was used instead of $LiNMe_2$. Yellow crystalline **3b** in 41% yield was isolated. IR (KBr pellet): ν_{CO} = 1599, 1545 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 14.44 (1588, 18.6 Hz), 13.77 (1858, 18.6 Hz). ^1H NMR ($CDCl_3$): δ 4.52, 3.18, 2.82, 2.21 (sextets, 14.0, 7.0 Hz, 4 H, NCH_2CH_3), 0.96, 0.39 (t, 7.0 Hz, 6 H, NCH_2CH_3).

Structural Determination of *cis*-Pt(COPh)$(CONEt_2)(PPh_3)_2$. Single crystals suitable for X-ray diffraction were obtained by slowly diffusing Et_2O into a concentrated CH_2Cl_2 solution of **3b** in a double-tube apparatus. Diffraction data were measured on a CAD-4 diffractometer with graphite-monochromated Cu Kα radiation at 300 K. Cell parameters were determinbed by a least-squares fit. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method. Atomic scattering factors were taken from ref 13. Computing programs are from the NRCC SDP VAX package. The crystal data are listed in Table I. The final atomic coordinates for non-hydrogen atoms are listed in Table II. The selected bond distances and the bond angles are collected in Table III. The ORTEP drawing of **3b** is shown in Figure 2. Other data are supplied in the supplementary material.

Decomposition of *cis*-Pt(COPh)$(CONEt_2)(PPh_3)_2$. A sample of 30 mg of complex **3b** stood in $CDCl_3$ at 35 °C. The decomposition was monitored by NMR spectroscopy and found to be completed in about 1 day. The inorganic and organic products were identified mainly by NMR spectroscopy and comparison to authentic samples with use of the coinjection method. Quantitative data were obtained by NMR integrations and also by comparison to the standards. The standard $PhCOCONEt_2$ was prepared by the reaction of PhCOCOCl and Et_2NH. Products are as follows. *trans*-Pt(COPh)(Cl)$(PPh_3)_2$: IR ($CDCl_3$) ν_{CO} = 1615 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 20.16 (3380 Hz). Et_2NH: ^1H NMR ($CDCl_3$) δ 1.10 (t, 7.1 Hz, NCH_2CH_3), 2.65 (q, 7.1 Hz, NCH_2CH_3). $PhCOCONEt_2$: ^1H NMR ($CDCl_3$, sample) δ 1.12, 1.20 (t, t, 7.2 Hz, NCH_2CH_3), 3.27, 3.37 (q, q, 7.2 Hz, NCH_2CH_3) ^1H NMR ($CDCl_3$, standard) δ 1.16, 1.30 (t, t, 7.2 Hz, NCH_2CH_3), 3.25, 3.57 (q, q, 7.2 Hz, NCH_2CH_3). $PhCONEt_2$: ^1H NMR ($CDCl_3$, standard) δ 1.48 (t, 7.2 Hz, NCH_2CH_3), 3.03 (sextet, 7.2 Hz, NCH_2CH_3).

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Note Added in Proof. After our submission of this paper, two articles of relevant contents have been independently reported: Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603, 2612.

Supplementary Material Available: Tables of all crystal data, atomic coordinates, bond lengths and bond angles, and thermal parameters (7 pages); a listing of structure factors (20 pages). Ordering information is given on any current masthead page.

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(12) Attempts to measure the energy barriers of the rotations were unsuccessful due to the thermal instability of **3b**.

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