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Platinum Carbenes Formed via Intramolecular Acyl–Carbamoyl Coupling in a Cis Carbamoyl α-Ketoacyl Complex of Platinum(II)

Jwu-Ting Chen,* Wen-Hwa Tzeng, Fu-Yu Tsai, Ming-Chu Cheng, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

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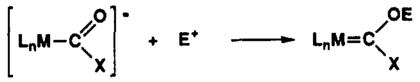
Summary: The isomerization of *trans*-Pt(COCOPh)(CONEt_2)$(PPh_3)_2$ (**1**) takes place in chloroform in the presence of CO at 1 atm, yielding the novel *cis*-Pt(COCOPh)(CONEt_2)$(PPh_3)_2$ (**2**) in over 80% yield. The addition of excess Et_2NH facilitates such isomerization and results in biphasic kinetics. The kinetics and the detection of an intermediate, Pt(COCOPh)($CONEt_2$)(CO)(PPh_3) (**4**), are consistent with a consecutive mechanism. The reaction of *cis*-Pt(COCOPh)($CONEt_2$)$(PPh_3)_2$ with iodine leads to the formation of several amino(acyloxy)carbenoid complexes, *trans*-*Pt*(C(NEt_2)(OC{O}Ph))(PPh_3)I_2 (**5a**), *cis*-Pt(C(NEt_2)(OC{O}Ph))(PPh_3)I_2 (**5b**), and *cis*-[Pt(C(NEt_2)(OC{O}Ph))(I)$(PPh_3)_2$](I) (**6**), presumably via oxidation-promoted intramolecular acyl–carbamoyl coupling.

A well-established synthetic route for the preparation of carbenoid complexes of the Fischer type is via electrophilic addition of a carbocation to the oxygen atom of an "acyl-type" ligand (eq 1).[1] Although acylation to metal–

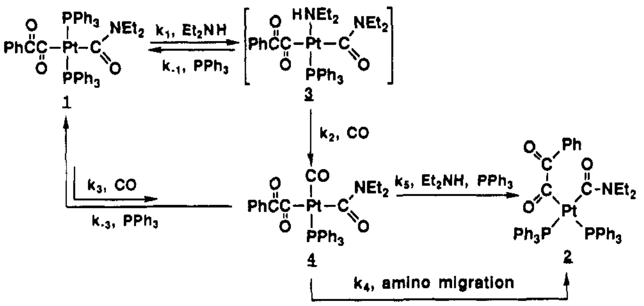


$$\left[L_nM{-}C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow X}\end{matrix}\right]^- + E^+ \longrightarrow L_nM{=}C\begin{matrix}{}^{\nearrow OE}\\{}_{\searrow X}\end{matrix} \qquad (1)$$

acyl species and the relevant mechanisms have been widely proposed in various reactions of carbene formation,[2] the well-characterized (acyloxy)carbenoid complexes (M=C-(OC{O}R)X) are still relatively rare.[3] We report here the formation of the first examples of amino(acyloxy)carbenoid complexes of platinum via an unprecedented intramolecular acyl–carbamoyl coupling in a novel cis α-ketoacyl carbamoyl complex of platinum(II).

We have previously reported the synthesis of *trans*-Pt(COCOPh)($CONEt_2$)$(PPh_3)_2$ (**1**) from the reaction of *trans*-[Pt(COCOPh)(CO)$(PPh_3)_2$](BF_4) with Et_2NH.[4] In $CHCl_3$ at 20 °C, complex **1** tends to decompose to *trans*-Pt(COCOPh)(Cl)$(PPh_3)_2$ and Et_2NH along with a few decarbonylated organometallic species, presumably by reaction with HCl in the solvent. In the presence of CO at 1 atm, in contrast, a solution of complex **1** (0.03 M) in chloroform or benzene at −20 °C isomerized to *cis*-Pt(COCOPh)($CONEt_2$)$(PPh_3)_2$ (**2**) to an extent of 1:4.5 and 1:3.3 trans/cis ratios, respectively, within a few days. This equilibrium ratio was also achieved by starting with the pure cis isomer. Complex **2** has been isolated from the trans–cis mixture by repeated recrystallization from Et_2O and characterized spectroscopically.[5]

Scheme I



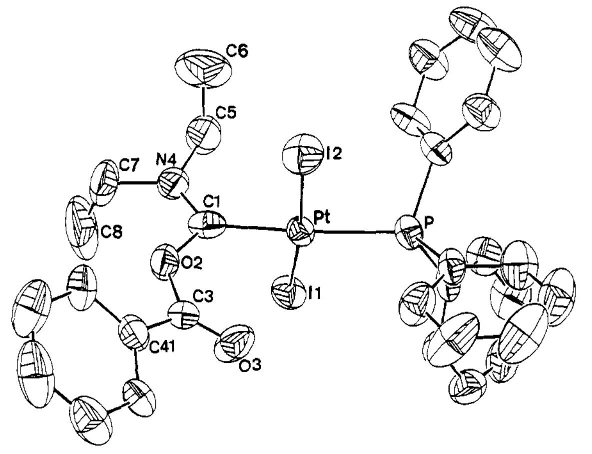


Figure 1. ORTEP drawing of complex **5a**. Selected bond distances (Å) and angles (deg): Pt–P = 2.297 (2), Pt–I1 = 2.612 (1), Pt–I2 = 2.617 (1), Pt–C1 = 1.969 (7), C1–O2 = 1.403 (8), C1–N4 = 1.324 (8), O2–C3 = 1.372 (7), C3–O3 = 1.195 (9), C3–C41 = 1.45 (1), N4–C5 = 1.460 (8), N4–C7 = 1.48 (1); I1–Pt–I2 = 173.26 (2), I1–Pt–P = 95.7 (6), I1–Pt–C1 = 86.2 (2), I2–Pt–P = 89.5 (5), I1–Pt–C1 = 88.5 (2), P–Pt–C1 = 176.7 (2), Pt–C1–O2 = 125.4 (4), Pt–C1–N4 = 128.3 (5), O2–C1–N4 = 106.3 (6), C1–O2–C3 = 123.0 (5), O2–C3–O3 = 121.8 (6), O2–C3–C41 = 112.7 (6), O3–C3–C41 = 125.5 (6), C1–N4–C5 = 119.1 (6), C1–N4–C7 = 125.8 (5), C5–N4–C7 = 115.1 (5). All H atoms are omitted.

The addition of Et_2NH remarkably enhanced the rates of isomerization, whereas it did not change the relative abundance of the two isomers in solution. The preliminary kinetic runs having $[Et_2NH]_0 \geq 20[\mathbf{1}]_0$ with CO at 1 atm in CH_2Cl_2 (saturated with CO) at 20 °C exhibit the biphasic plots of ln $(D_t - D_\infty)$ versus time, and the apparent rate constants of both stages are first order in $[Et_2NH]$.[6]

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(1) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983.

(2) (a) Hegedus, L. S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; NATO ASI Series 269; Kluwer: Dordrecht, The Netherlands, 1989; p 233. (b) Dötz, K. H.; Grotjahn, D.; Harms, K. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1384. (c) Wulff, W. D.; Dragisch, V.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* 1989, *8*, 2196.

(3) (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc. D* 1971, 570; *J. Chem. Soc. A* 1971, 3368. (b) Fischer, E. O.; Selmayr, T.; Kreissl, F. R. *Chem. Ber.* 1977, *110*, 2947.

(4) Huang, T.-M.; You, Y.-J.; Yang, C.-S.; Tzeng, W.-H.; Chen, J.-T.; Cheng, M.-C.; Wang, Y. *Organometallics* 1991, *10*, 1020.

(5) Selected spectral data for **2**: UV–vis ($CDCl_3$) λ_{max} = 474 nm, ϵ = 114 ± 5 M^{-1} cm^{-1}; IR (KBr) ν_{CO} = 1672, 1611, 1535 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 16.14 (J_{P-Pt} = 1920, J_{P-P} = 18.3 Hz), 13.65 (J_{P-Pt} = 1716, J_{P-P} = 18.3 Hz); ^1H NMR ($CDCl_3$) δ 0.29, 1.01 (3 H, t, 7.0 Hz), 2.12, 2.61, 3.15, 4.49 (1 H, sex, 13.7, 7.0 Hz). Anal. Calcd for $C_{49}H_{45}NO_3P_2Pt$: C, 61.76; H, 4.76; N, 1.47. Found: C, 60.99; H, 4.83; N, 1.47.

(6) Reaction runs with $[\mathbf{1}]_0 = 5.2 \times 10^{-3}$ M, $[CO]_0 = 8.5 \times 10^{-3}$ M,[7] and $[Et_2NH]_0 = (20–100)[\mathbf{1}]_0$ at 25 °C were done by monitoring the decreasing absorbance at 578 nm. Biphasic plots of ln $(D_t - D_\infty)$ versus time lasting at least 4 half-lives were obtained.[8] Thus, $k_f = k_3[CO] + k_1[Et_2NH]$ ($k_3[CO] = 0.0202\ s^{-1}$, $k_1 = 0.0344\ s^{-1}$) and $k_s = k_4 + k_5[Et_2NH]$ ($k_4 = 3.90 \times 10^{-4}\ s^{-1}$, $k_5 = 3.90 \times 10^{-3}\ s^{-1}$) were determined, respectively. Detailed results and the experimental procedure are given in the supplementary material.

(7) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. 3, p 265.

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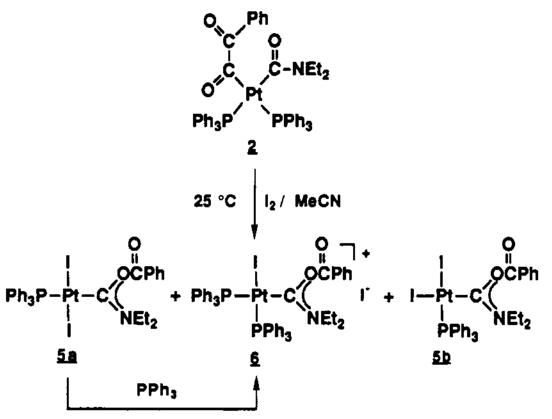
Scheme II



When PPh_3 was added in a 9-fold excess, only the slower stage in first-order kinetics was observed. An intermediate (with its maximum proportion ca. 15% of $[1]_0$) was detected spectroscopically in this reaction and has been assigned as $Pt(COCOPh)(CONEt_2)(CO)(PPh_3)$ (**4**) accordingly.[9] Such results are consistent with a consecutive mechanism as written in Scheme I.[10]

The addition of 2 equiv of iodine to complex **2** in benzene-d_6 at 21 °C results in instantaneous formation of an (acyloxy)carbenoid complex, *trans*-$Pt(C(NEt_2)(OC\{O\}Ph))(PPh_3)I_2$ (**5a**), in over 90% yield. The infrared spectrum of **5a** showed the stretching absorption of the benzoyl carbonyl at 1754 cm^{-1} and the carbene carbonyl at 1559 cm^{-1}. Its ^{31}P NMR resonance appeared at δ 8.38 with $J_{P-Pt} = 2490$ Hz. The ^1H NMR spectrum of **5a** comprises the amino methylene protons at δ 3.79 and 4.53 and the amino methyl protons at δ 1.36 and 1.52.[11] The structure of **5a** has been confirmed by X-ray crystallography.[12] According to its ORTEP drawing, shown in Figure 1, the amino(acyloxy)carbenoid ligand is disposed trans to the phosphine in a square-planar geometry. The carbenoid features of **5a** are comparable with those of an anilinoethoxycarbenoid complex.[14] The carbenoid plane N4–C1–O2 is nearly perpendicular to the coordination plane of the Pt, C1–I1–P–I2, with the dihedral angle being 101.1 (2)°. The dihedral angle between the N4–C1–O2 and the O2–C3–O3 planes is 21.4 (4)°.

The ready replacement of an iodide ligand in **5a** by PPh_3 leads to *cis*-$[Pt(C(NEt_2)(OC\{O\}Ph))(I)(PPh_3)_2](I)$ (**6**), in which the amino methylene protons are diastereotopic, appearing at δ 3.48, 3.64, 4.33, and 5.05 as sextets in the ^1H NMR spectrum. The two phosphorus atoms have distinct P–Pt couplings of 2355 and 3664 Hz, which were observed at δ 3.85 and 7.52, respectively, in the ^{31}P NMR spectrum.[15] Heterogeneously mixing equimolar amounts of complex **2** and iodine in acetonitrile at 25 °C causes the instantaneous evolution of gas and a color change from orange to light yellow, indicating the decarbonylation of the benzoylformyl ligand. The ^{31}P NMR data showed that **5a** and **6** were formed in a 1:2 ratio (60% total yield). Meanwhile, *trans*-$Pt(COCOPh)(I)(PPh_3)_2$ (20%) and *trans*-$Pt(COPh)(I)(PPh_3)_2$ (18%) were also produced, along with a trace of $PhCONEt_2$ and $PhCOCONEt_2$.[16,17] When I_2 in more than double molar proportion was employed, another carbene complex, **5b** (cis isomer of **5a**), was also observed in <10% yield in addition to **5a** and **6** on the basis of the NMR data (Scheme II).[18] No similar transformation was found for the trans complex **1**.

The platinum carbene complexes are likely formed from an iodine-promoted intramolecular coupling between the carbamoyl and the benzoylformyl ligands through the formation of a C–O bond with concomitant loss of CO from the latter ligand. An alternative mechanism involving coupling between the carbamoyl ligand and a benzoyl group that results from the decarbonylation of the benzoylformyl ligand cannot be totally excluded, because treatment of *cis*-$Pt(COPh)(CONEt_2)(PPh_3)_2$ with I_2 also provides carbenoid complex **5a** as a minor product. The oxidative addition of I_2 to **2** apparently facilitates the carbenoid formation. It is not immediately clear whether I_2 was incorporated before or after the acyl–carbamoyl coupling. Further mechanistic investigation of these remote couplings is in progress.

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Supplementary Material Available: Kinetic data and plots for the isomerization between **1** and **2** and tables of complete crystal data, complete bond lengths and angles, atomic coordinates, and thermal parameters and a figure with complete atomic labeling for **5a** (10 pages); a listing of structure factors for **5a** (15 pages). Ordering information is given on any current masthead page.

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[8] Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn & Bacon: Boston, 1974.

[9] Selected spectral data for **4**: IR (CH_2Cl_2) $\nu_{CO} = 2080, 1573\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 16.18 ($J_{P-Pt} = 1921$ Hz).

[10] Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2612.

[11] Selected spectral data for **5a**: IR (KBr) $\nu_{CO} = 1754, 1559\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 8.38 ($J_{P-Pt} = 2490$ Hz); ^1H NMR ($CDCl_3$) δ 1.36, 1.52 (3 H, t, 7.2 Hz) and δ 3.79, 4.53 (2 H, q, 7.2 Hz).

[12] Crystal data for **5a**: $C_{30}H_{30}O_2NPI_2Pt$, $P2_12_12_1$, $a = 12.752$ (6) Å, $b = 14.994$ (6) Å, $c = 16.381$ (7) Å, $\alpha = \beta = \gamma = 90°$, $V = 3132$ (2) Å^3, $Z = 4$, $\mu = 5.58\ mm^{-1}$, determined on a CAD-4 diffractometer at $T = 298$ K, λ(Mo Kα) = 0.7107 Å, $\theta_{max} = 45°$, 4101 total reflections, 3712 observed reflections ($I > 2.0\sigma(I)$), $R = 0.023$, $R_w = 0.017$ obtained by least-squares refinement. The computing program is the NRCC SDP VAX package.[13]

[13] Gabe, E. J.; Lee, F. L.; LePage, Y. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.

[14] Badley, E. M.; Muir, K. W.; Sim, G. A. *J. Chem. Soc. A* **1971**, 1930.

[15] Selected spectral data for **6**: IR (NaCl) $\nu_{CO} = 1752, 1566\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 3.85 ($J_{P-Pt} = 3664$, $J_{P-P} = 21.5$ Hz), 7.52 ($J_{P-Pt} = 2355$, $J_{P-P} = 21.5$ Hz); ^1H NMR ($CDCl_3$) δ 1.12, 1.65 (3 H, t, 7.0 Hz), 3.46, 3.64, 4.33, 5.05 (1 H, m).

[16] Selected spectral data for *trans*-$Pt(COCOPh)(I)(PPh_3)_2$: IR (KBr) $\nu_{CO} = 1663, 1644\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 15.21 ($J_{P-Pt} = 3223$ Hz). Selected spectral data for *trans*-$Pt(COPh)(I)(PPh_3)_2$: $\nu_{CO} = 1623\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 16.94 ($J_{P-Pt} = 3316$ Hz). Selected spectral data for $PhCOCONEt_2$: $\nu_{CO} = 1676, 1635\ cm^{-1}$; ^1H NMR ($CDCl_3$) δ 1.13, 1.26 (3 H, t, 7.1 Hz), 3.22, 3.54 (2 H, q, 7.1 Hz).[17]

[17] Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1991**, *10*, 175.

[18] Selected spectral data for **5b**: IR (KBr) $\nu_{CO} = 1763, 1545\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 6.03 ($J_{P-Pt} = 3821$ Hz); ^1H NMR ($CDCl_3$) δ 1.08, 1.32 (3 H, t, 7.2 Hz), 3.14, 3.31, 3.81, 4.83 (1 H, sex, 14.1, 7.2 Hz).