Di-, Tri- and Tetra-nuclear Palladium(II) Complexes with Ureido Bridging Groups

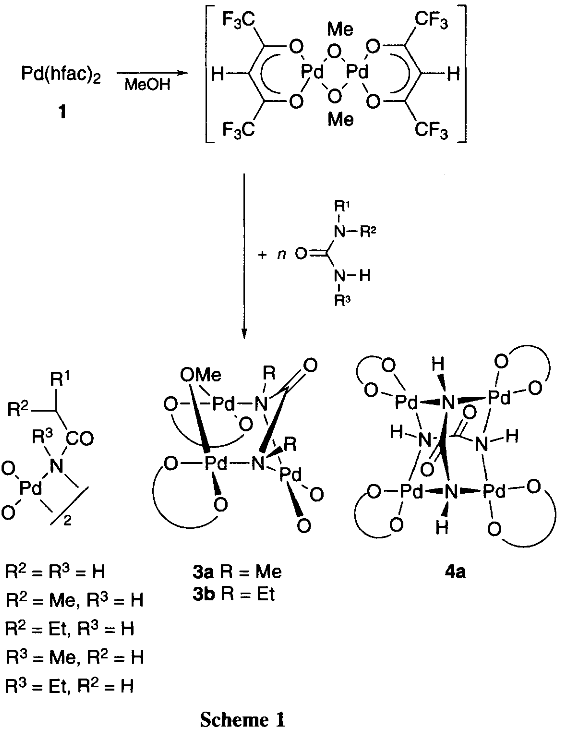
Seichi Okeya,*[a] Shouzou Koshino,[a] Miho Namie,[a] Isoroku Nagasawa[b] and Yoshihiko Kushi[b]

[a] *Faculty of Education, Wakayama University, Sakaedani, Wakayama 640, Japan*
[b] *Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*

The reaction of [Pd(hfac)$_2$] (Hhfac = hexafluoroacetylacetone) with ureas in MeOH gives di-, tri- and tetra-nuclear palladium(II) complexes with hfac chelates and ureido(1− or 2−) bridges.

Urea is a final product of the nitrogen cycle in the human body and many bio-chemically important substances have an N(CO)N skelton, such as uracil, cytosine and thymine. Urea is also important as a nitrogen fertilizer and a starting material for the preparation of pharmaceuticals and resins. Urea and its alkyl or aryl derivatives act as weak N- or O-donors to metals,[1] but the ureido(1−) anion functions as an *N*-bonded monodentate[2] or an *N,O*-chelating ligand[1a] and the ureido(2−) anion acts as an *N,N′*-chelating[3] or a μ_2-bridging ligand with various bonding modes.[3a,b,4] We now report the preparation of di-, tri- and tetra-nuclear Pd complexes containing new μ_2-ureido(1−), μ_3- or μ_4-ureido(2−) bridges.

When urea (0.19 mmol) was added to a MeOH solution (1 ml) of [Pd(hfac)$_2$] **1** (0.19 mmol) at room temperature, [Pd(hfac)(μ-*N*HCONH$_2$)]$_2$ **2a** was immediately deposited as a yellow precipitate in 70% yield (Scheme 1).† Under similar reaction conditions, 1,1-dimethyl- and 1,1-diethyl-urea gave complexes **2b** (73%) and **2c** (after SiO$_2$ chromatography, 94%) respectively. Similar amido-bridged aniline[5] and 2-thienylamine[6] complexes with Pd^{II} have been reported. While excess of 1,3-dimethyl- and 1,3-diethyl-urea reacted with **1** in MeOH to afford complexes **2d** (after SiO$_2$ chromatography, 32%) and **2e** (trace) respectively, 0.5 equiv. gave dark red plates of [Pd$_3$(hfac)$_3$(μ_3-R*N*CO*N*R)(μ_2-OMe)] (**3a**: R = Me, after SiO$_2$ chromatography, 28%, **3b**: R = Et, 79%). In contrast, when 0.5 equiv. of urea (0.097 mmol) was added to a MeOH solution (2 ml) of **1** (0.19 mmol) at room temperature and the resulting mixture was left to stand overnight, orange crystals of [Pd$_2$(hfac)$_2$(μ_4-*N*HCO*N*H)]$_2$ **4a** were deposited in 81% yield. An intermediate in these reactions seems to be [Pd(hfac)(μ-OMe)]$_2$,[7] because the ureas did not react with **1** in other solvents. The driving force for these complexation reaction of ureas is the strong deprotonating ability of the μ-OMe ligand. Pd(acac)$_2$ did not react with ureas in any organic solvents.



2a R^1 = R^2 = R^3 = H
2b R^1 = R^2 = Me, R^3 = H
2c R^1 = R^2 = Et, R^3 = H
2d R^1 = R^3 = Me, R^2 = H
2e R^1 = R^3 = Et, R^2 = H

3a R = Me
3b R = Et

4a

Scheme 1

The ureido (1− or 2−) anion in these new complexes coordinates Pd^{II} only through its N-donor atoms; its IR spectrum shows a strong band at 1670–1750 cm^{-1} assigned to urea ν_{CO}.[1a,c,3a,8] NMR spectra reveal that each hfac unit in these complexes retains its *O,O′*-chelating structure.[9] The ^{1}H NMR

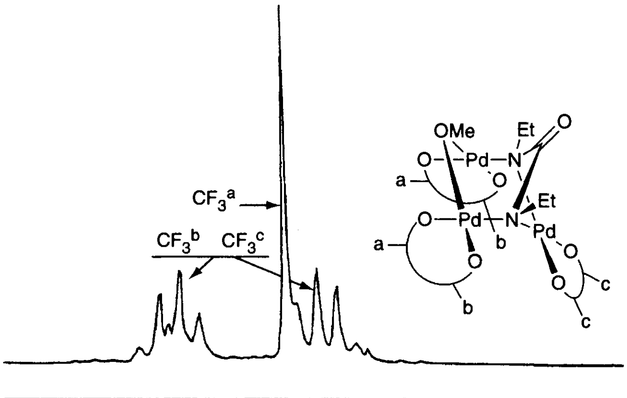


Fig. 1 ^{19}F NMR spectrum of **3b** in CDCl$_3$ (ext. C$_6$F$_6$)

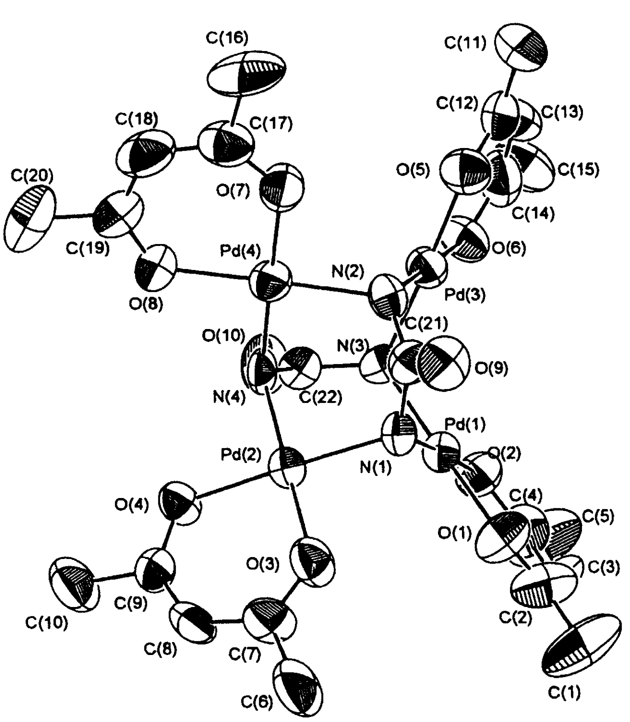


Fig. 2 Structure of **4b** with hydrogen atoms omitted for clarity. Selected structural parameters, Pd(1)–N(1) 2.048(12), Pd(1)–N(3) 2.017(13), Pd(1)–O(1) 1.985(13), Pd(1)–O(2) 2.009(13), Pd(2)–N(1) 2.056(12), N(1)–C(21) 1.41(3), N(2)–C(21) 1.34(3), O(9)–C(21) 1.24(3) Å, N(1)–Pd(1)–N(3) 93.7(6), O(1)–Pd(1)–O(2) 93.8(6), N(1)–Pd(1)–O(1) 85.8(6), N(3)–Pd(1)–O(2) 86.8(6), Pd(1)–N(1)–Pd(2) 95.9(6), Pd(1)–N(1)–C(21) 120.2(10), Pd(2)–N(1)–C(21) 117.9(10), Pd(3)–N(2)–Pd(4) 99.7(6), N(1)–C(21)–N(2) 121.3(14), O(9)–C(21)–N(1) 116.1(15), O(9)–C(21)–N(2) 122.5(16)°.

spectrum of **3b** shows that the two Et groups in the ureido dianion are equivalent but that their methylene protons are in a diastereotopic environment. The two ^1H and ^{13}C signals assigned to CH in hfac appear in an intensity ratio of 2 : 1, indicating that there are three hfac clelates and two of them are equivalent. On the other hand the ^{13}C NMR spectrum of **3** shows the existence of three types of $COCF_3$ group in the same intensity ratio, indicating that one hfac is in a symmetrical and the others are in an unsymmetrical environment. From these findings a trinuclear structure with μ_2-methoxo and μ_3-ureido-(2−) bridges is suggested for **3**. The ^{19}F NMR spectrum of **3** (Fig. 1) demonstrates that the six-membered ring containing three Pd atoms exists in the chair conformation, since there are three types of CF_3 signal and two of them are through-space-coupled. NMR spectra for **4a** are quite simple, reflecting its high symmetry. Molecular weight data strongly suggest multinuclear structures of **2**, **3** and **4**.

Suitable crystals for X-ray analysis could not be obtained for **4a**. The ligand hfac in complex **4a** can be easily exchanged with acac. Compound **4a** (0.355 mmol) was dissolved in warm acetylacetone (20 ml). Diethyl ether (50 ml) was added and the mixture was left to stand for several weeks, forming red crystals of $[Pd_2(acac)_2(\mu_4\text{-}N\text{HCO}N\text{H})]_2 \cdot Et_2O$ **4b** in 74% yield. The X-ray crystal structure (Fig. 2)‡ of **4b** confirmed its novel tetranuclear structure. The structure of the complex consists of four acetylacetonatopalladium(II) units joined by two ureido-(2−) bridges that are perpendicular to each other. Four Pd atoms are located at the corners of a square plane. The coordination geometry of the N_2O_2 donor around each Pd atom is almost planar. The Pd–N and Pd–O bond distances are normal. There is no Pd–Pd bond since the average Pd–Pd distance is 3.17 Å.

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Footnotes

† *N*HCONH$_2$ = *N*-bonded urea; R*N*CO*N*R = *N,N′*-bonded. All new compounds gave satisfactory elemental analyses and were characterised by spectroscopy and molecular weight measurement (vapour pressure osmometry). *Selected data, e.g.* for **2b**: ^1H NMR (60 MHz, $CDCl_3$) δ 2.65 (s, 6H, NCH_3), 2.98 (d, 6H, ^3J 5 Hz, $HNCH_3$), 6.10 (s, 2H, hfac-CH), 8.03 (br. q, 2H, ^3J 5 Hz, NH); ^{13}C NMR (15 MHz, $CDCl_3$) δ 28.4, 42.0 (NCH_3), 92.4 (hfac-CH), 116.1 (q, $^1J_{C\text{-}F}$ 284 Hz, hfac-CF_3), 166.3 (urea-CO), 174.9 (q, $^2J_{C\text{-}F}$ 36 Hz, hfac-CO); ^{19}F NMR (84 MHz, $CDCl_3$, ext. C_6F_6) δ 92.4; IR (KBr) ν/cm^{-1} 1695 (ν_{CO}, urea); M (CH_2Cl_2): found 846; calc. 801. For **3b**: ^1H NMR (400 MHz, $CDCl_3$); δ 1.57 (t, 6H, ^3J 7 Hz, CH_2CH_3), 2.60, 2.72 (AB q of q, each 1H, $^2J_{gem}$ 13, $^3J_{vic}$ 7 Hz, CH_2CH_3), 2.60 (s, 3H, OCH_3), 6.17 (s, 1H, hfac-CH), 6.32 (s, 2H, hfac-CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5 (CH_2CH_3), 46.1 (OCH_3), 57.9 (CH_2CH_3), 92.3, 93.9 (intensity ratio 1 : 3, hfac-CH), 115.6, 115.9, 116.8 (each q, intensity ratio 1 : 1 : 1, $^1J_{C\text{-}F}$ 284 Hz, hfac-CF_3), 175.5, 175.6, 175.7 (each q, intensity ratio 1 : 1 : 1, $^2J_{C\text{-}F}$ 36 Hz, hfac-CO), 176.3 (urea-CO); ^{19}F NMR (84 MHz, $CDCl_3$, ext. C_6F_6) δ 92.1, 92.7 (each q, through-space-$J_{F\text{-}F}$ 7 Hz), 92.3 (s); IR (KBr) ν/cm^{-1} 1745 (ν_{CO}, urea); M (CH_2Cl_2): found 1060; calc. 1085. For **4a**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 4H, NH), 6.40 (s, 4H, hfac-CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.6 (hfac-CH), 115.7 (q, $^1J_{C\text{-}F}$ 284 Hz, hfac-CF_3), 173.0 (urea-CO), 175.8 (q, $^2J_{C\text{-}F}$ 37 Hz, hfac-CO); ^{19}F NMR (84 MHz, $CDCl_3$, ext. C_6F_6) δ 93.0; IR (KBr) ν/cm^{-1} 1682 (ν_{CO}, urea); M (CH_2Cl_2): found 1351; calc. 1370. For **4b** (after removing Et_2O by pumping): ^1H NMR (60 MHz, $CDCl_3$) δ 1.96 (s, 24H, acac-CH_3), 2.66 (br, 4H, NH), 5.40 (s, 4H, acac-CH); ^{13}C NMR (15 MHz, $CDCl_3$) δ 25.6 (acac-CH_3), 101.1 (acac-CH), 178.3 (urea-CO), 186.1 (acac-CO); IR (KBr) ν/cm^{-1} 1672 (ν_{CO}, urea); M (CH_2Cl_2): found 891; calc. 938.

‡ *Crystal data* for **4b**: $C_{26}H_{42}N_4O_{11}Pd_4$, M = 1010.25, monoclinic, a = 23.575(8), b = 15.829(9), c = 12.222(8) Å, β = 93.06(4)°, U = 4554(4) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.47 g cm^{-3}, μ(Mo-Kα) = 15.7 cm^{-1}, $F(000)$ = 1992, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, room temperature. All crystallographic measurements were made using a MAC Science MXC3 diffractometer. Empirical absorption corrections (Ψ-scan) were applied. Lattice parameters were determined from the positions of 22 reflections. Data were measured in the range $2\theta \leqslant 50°$ in the ω–2θ scan mode with three check reflections being measured every 100 data. The structure was solved by direct methods and refined by full-matrix least-squares analysis using 4367 unique reflections (total reflections 6018) to final a R = 0.0791, R_w = 0.0860 (C. Gilmore, N. Stewart and C. Edwards, Crystan-GM Program for Crystal Structure Refinement, The University of Glasgow, Scotland, and MAC Science Co Ltd, Yokohama, Japan, 1994). Hydrogen atoms placed at calculated positions (ether hydrogen atoms were neglected). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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