CHEMISTRY LETTERS, pp. 1127-1130, 1994.

Ligand Exchange Reactions of Thienylene-Bridged Dinuclear Platinum Complex with Diphosphines. Synthesis and Molecular Structure of Diphosphine-Bridged μ-2, 5-Thienylene Diplatinum Complex

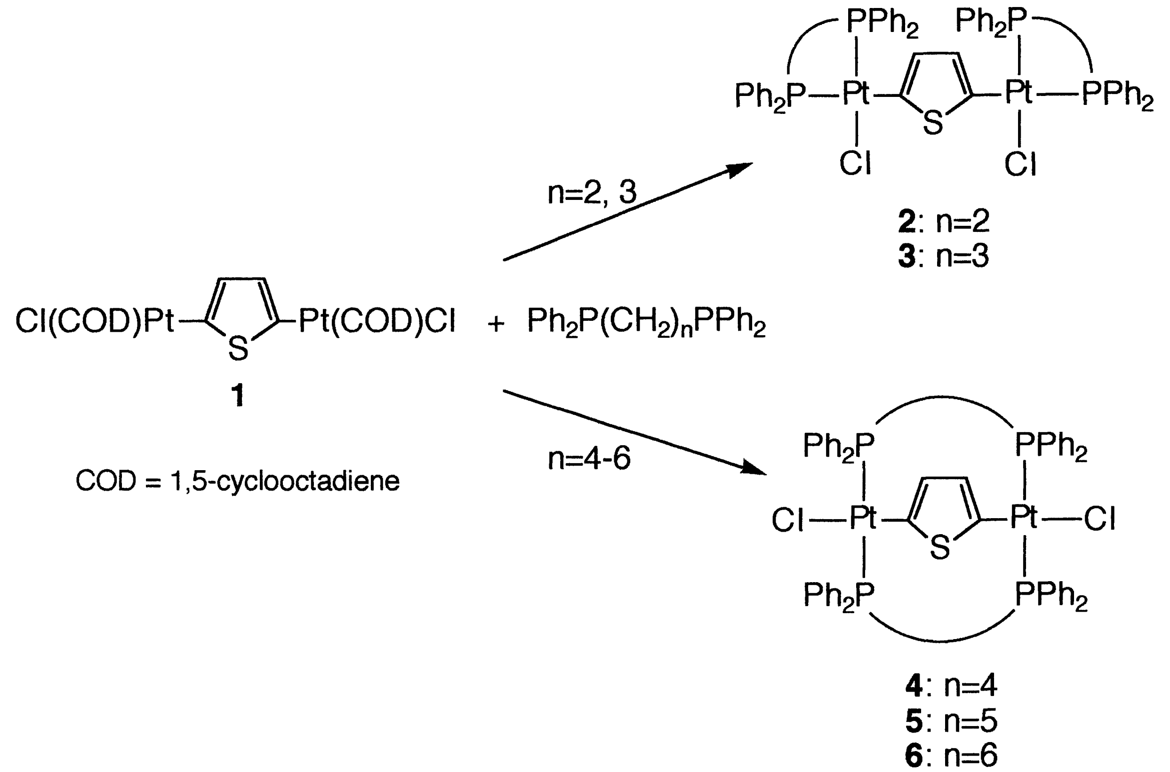
Sonae KOTANI, Tomohiro ADACHI,† Toshikatsu YOSHIDA,† Kiyotaka ONITSUKA,
and Kenkichi SONOGASHIRA*
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558
† Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai,
Osaka 591

While treatment of bis{chloro(1,5-cyclooctadiene)platinum(II)}-μ-2, 5-thienylene (**1**) with bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$, having a short methylene chain (n=2, 3) leads to the formation of diphosphine-chelate diplatinum complexes, in the reactions of **1** with diphosphines having a long alkyl chain (n=4, 5, 6), diphosphine-bridged diplatinum complexes were produced. The molecular structure of the complex, in which two platinum atoms are bridged by two 1, 6-bis(diphenylphosphino)hexane ligands and 2, 5-thienylene group, was determined by a single-crystal X-ray diffraction study.

Linking transition metal atoms together with π-conjugated groups allows the d_π-p_π interactions between them, and many transition metal complexes having π-conjugated groups were prepared.[1)] Although thiophene derivatives have received much attention as an intermediate for the synthesis of conductive polymers,[2)] there are few reports on the complexes bridged by heterocyclic groups.[3)] Recently, we have reported the syntheses and properties of 2, 5-thienylene- and 2, 5'-dithienylene-bridged diplatinum complexes.[4)]

Ligand exchange reaction is one of the basic reactions in organometallic chemistry. In the case of the reaction of a mutinuclear complex with a bidentate ligand, it is of interest that the ligand acts as not only a chelating ligand but also a bridging ligand.[5)] Thus, we wish to describe here the ligand exchange reactions of bis{chloro(1,5-cyclooctadiene)platinum(II)}-2, 5- thienylene (**1**) with bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ (n=2-6).

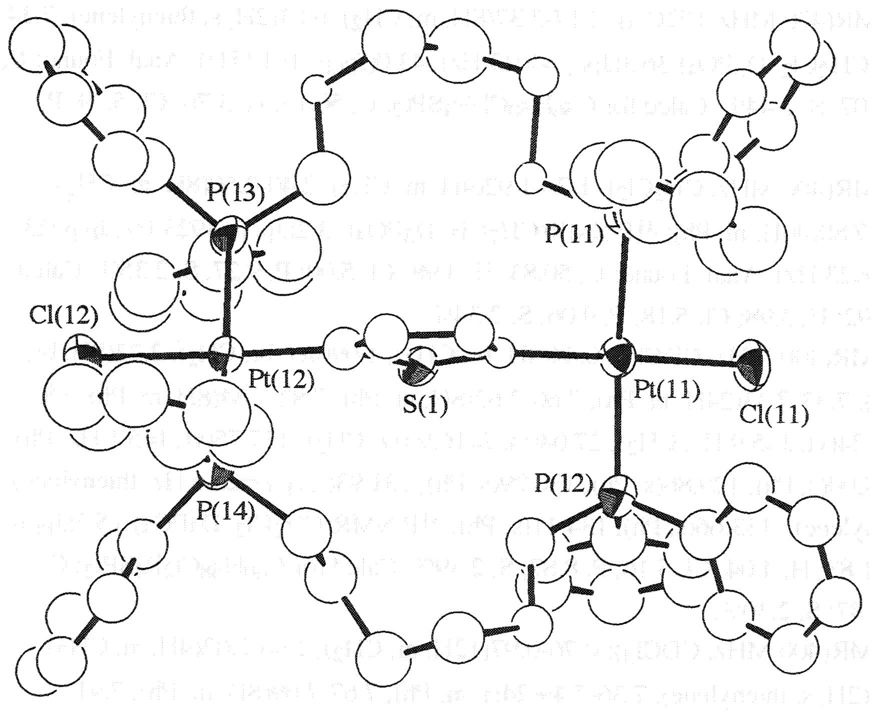
Complex **1** was treated with two equivalents of 1, 2-bis(diphenylphosphino)ethane (dppe) in dichloromethane at room temperature to give pale yellow micro crystals (**2**)[6)] in 91% yield. The ^{1}H NMR spectrum of **2** suggested that cyclooctadiene was exchanged by dppe, which was supported by an elemental analysis. In the FAB mass spectrum molecular ion (m/z 1340) was detected, and in the ^{31}P NMR spectrum two singlets were observed at δ 43.4 ($J_{Pt\text{-}P}$=1910 Hz) and 36.7 ($J_{Pt\text{-}P}$=4043 Hz) having attendant satellites due to the coupling with ^{195}Pt nucleus. From these spectroscopic data complex **2** was characterized as a thienylene-bridged diplatinum complex, in which the dppe ligands chelate to each platinum atom mononuclearly in a *cis* configuration. Similar reaction of **1** with 1, 3-bis(diphenylphosphino)propane (dppp) also gave mononuclearly chelated complex (**3**)[7] in 91% yield.



Scheme 1.

On the other hand, treatment of **1** with 1,4-bis(diphenylphosphino)butane (dppb) also caused the ligand exchange reaction to give pale yellow needles (**4**)[8] in 76% yield, of which ^{31}P NMR spectrum exhibited one singlet at δ 15.7 with satellite signals (J_{Pt-P}=2871 Hz). Though the ^{31}P NMR data suggest that phosphorus atoms are bonded to the platinum in a *trans* configuration, the alkyl chain of dppb is so short that the ligand is not able to coordinate to the platinum atom as a *trans* chelate ligand. In the FAB mass spectrum molecular ion (m/z 1396) was detected, indicating that dppb does not bridge intermolecularly to produce a poly-nuclear complex but coordinate intramolecularly. Therefore, these data suggest that the dppb ligands, as well as the 2, 5-thienylene group, bridge two platinum atoms. When complex **1** was treated with 1, 5-bis(diphenylphosphino)pentane (dpppe) and 1, 6-bis(diphenylphosphino)hexane (dpph), diphosphine-bridged complexes **5**[9] and **6**[10] were obtained in 76 and 83% yields, respectively. In all of the above ligand exchange reactions, any polymeric complex, in which diphosphine bridged intermolecularly, was not obtained.

In order to determine the presence of bridging diphosphine ligands, an X-ray diffraction analysis of **6** was carried out.[11] Two independent molecules with essentially the same structures are contained in a unit cell, and one of them is presented in Fig. 1 with the selected bond distances and angles. The Pt-C distances are 1.99(4) and 2.08(3) Å, which are in the range of the normal Pt-C(sp^2) bond length.[12] The dihedral angle between two Pt coordination planes is 48.6° and the two Pt coordination planes twist to the thienylene ring by 106.0° and 68.7°, respectively.



Pt(11)-Cl(11)	2.38(1)
Pt(11)-P(11)	2.32(2)
Pt(11)-P(12)	2.32(1)
Pt(11)-C(11)	2.08(3)
Pt(12)-Cl(12)	2.38(1)
Pt(12)-P(13)	2.29(1)
Pt(12)-P(14)	2.31(1)
Pt(12)-C(14)	1.99(4)
Cl(11)-Pt(11)-C(11)	178(1)
P(11)-Pt(11)-C(11)	88(1)
P(12)-Pt(11)-C(11)	92(1)
Cl(12)-Pt(12)-C(14)	176(1)
P(13)-Pt(12)-C(14)	93(1)
P(14)-Pt(12)-C(14)	89(1)

Fig. 1. Molecular structure of complex **6** with selected bond distances(Å) and angles(°).

It is noteworthy that in the diphosphine-bridged complexes the signals assigned to the methylene protons of diphosphine except α protons to the phosphorus are as follows, **4**: δ 0.44, 1.09; **5**: δ 0.76-0.97; **6**: δ 1.06, respectively. These signals are observed in higher magnetic fields than the normal methylene chemical shifts owing to the shielding effect of thienylene group, and the shorter the alkyl chain of diphosphine is, the larger the magnitude of shift is.

Further studies are now in progress. This work was supported in part by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics (No. 05236106) from the Ministry of Education, Science and Culture.

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6) mp 203-205 °C (dec.); ^{1}H NMR(400 MHz, $CDCl_3$): 2.17-2.37(8H, m, CH_2), 6.03(2H, s, thienylene), 7.34-7.96(40H, m, Ph); ^{31}P NMR(CH_2Cl_2, D_3PO_4) 36.3(J_{Pt-P}=4043 Hz), 43.0(J_{Pt-P}=1910 Hz); Anal. Found: C, 49.98; H, 3.86; Cl, 5.11; P, 9.07; S, 2.44%. Calcd for $C_{56}H_{50}Cl_2P_4SPt_2$: C, 50.19; H, 3.76; Cl, 5.29; P, 9.25; S, 2.39%.

7) mp 268-270 °C (dec.); ^{1}H NMR(400 MHz, CD_2Cl_2): 1.76-1.92(4H, m, CH_2), 2.40-2.50(8H, m, CH_2), 5.49(2H, s, thienylene), 7.19-7.80(40H, m, Ph); ^{31}P NMR(CH_2Cl_2, D_3PO_4) -3.2(J_{Pt-P}=3923 Hz, J_{P-P}=23 Hz), -0.4(J_{Pt-P}=1783 Hz, J_{P-P}=23 Hz); Anal. Found: C, 50.83; H, 3.98; Cl, 5.00; P, 9.27; S, 2.35%. Calcd for $C_{58}H_{54}Cl_2P_4SPt_2$: C, 50.92; H, 3.98; Cl, 5.18; P, 9.06; S, 2.34%.

8) mp 276-280 °C (dec.); ^{1}H NMR(400 MHz, $CDCl_3$): 0.44(4H, br, CH_2), 1.09(4H, br, CH_2), 2.22(8H, br, CH_2), 6.61(2H, s, thienylene), 7.33-7.43(24H, m, Ph), 7.60-7.62(8H, m, Ph), 7.82-7.84(8H, m. Ph); ^{13}C NMR(100 MHz, $CDCl_3$): 26.24(vt, J=5.9 Hz, CH_2), 27.04(vt, J=16.9 Hz, CH_2), 127.75(vt, J=5.1 Hz, Ph), 128.22(vt, J=4.4 Hz, Ph), 129.00(s, Ph), 129.86(s, Ph), 130.29(s, Ph), 131.93(t, J_{P-C}=25.6 Hz, thienylene), 132.18(t, J_{P-C}=26.4 Hz, thienylene), 133.66(s, Ph), 134.11(s, Ph); ^{31}P NMR(CH_2Cl_2, D_3PO_4) 15.7(J_{Pt-P}= 2871 Hz); Anal. Found: C, 51.83; H, 4.04; Cl, 5.16; P, 8.87; S, 2.39%. Calcd for $C_{60}H_{58}Cl_2P_4SPt_2$: C, 51.62; H, 4.19; Cl, 5.08; P, 8.87; S, 2.30%.

9) mp 292-296 °C (dec.); ^{1}H NMR(400 MHz, $CDCl_3$): 0.76-0.97(12H, m, CH_2), 1.96-2.02(4H, m, CH_2), 2.16-2.27(4H, m, CH_2), 6.35(2H, s, thienylene), 7.36-7.49(24H, m, Ph), 7.67-7.69(8H, m, Ph), 7.91-7.94(8H, m, Ph); ^{13}C NMR(100 MHz, $CDCl_3$): 19.96(s, CH_2), 26.83(vt, J=19.0 Hz, CH_2), 30.58(vt, J=8.1 Hz, CH_2), 127.72(s, Ph), 128.10(s, Ph), 129.67(s, Ph), 129.98(s, Ph), 130.24(s, Ph), 131.20(t, J_{P-C}=26.4 Hz, thienylene), 132.43(t, J_{P-C}=27.1 Hz, thienylene), 133.65(s, Ph), 134.32(s, Ph); ^{31}P NMR(CH_2Cl_2, D_3PO_4) 14.4(J_{Pt-P}=2804 Hz); Anal. Found: C, 52.07; H, 4.35; Cl, 5.18; P, 8.43; S, 2.35%. Calcd for $C_{62}H_{62}Cl_2P_4SPt_2$: C, 52.29; H, 4.39; Cl, 4.98; P, 8.70; S, 2.25%.

10) mp 251-253 °C; ^{1}H NMR(400 MHz, $CDCl_3$): 1.06(16H, br, CH_2), 1.92-2.09(8H, m, CH_2), 6.27(2H, s, thienylene), 7.37-7.42(24H, m, Ph), 7.69-7.80(16H, m, Ph); ^{13}C NMR(100 MHz, $CDCl_3$): 22.03(s, CH_2), 24.96(vt, J=17.6 Hz, CH_2), 27.01(vt, J=6.6 Hz, CH_2), 127.84(s, Ph), 129.86(s, Ph), 129.91(s, Ph), 130.65(t, J_{P-C}=26.4 Hz, thienylene), 131.36(t, J_{P-C}=27.1 Hz, thienylene), 133.94(s, Ph), 134.00(s, Ph), 134.06(s, Ph); ^{31}P NMR(CH_2Cl_2, D_3PO_4) 14.2(J_{Pt-P}=2803 Hz); Anal. Found: C, 52.79; H, 4.41; Cl, 5.16; P, 8.61; S, 2.05%. Calcd for $C_{64}H_{66}Cl_2P_4SPt_2$: C, 52.39; H, 4.58; Cl, 4.88; P, 8.53; S, 2.20%.

11) Crystals of complex **6** suitable for an X-ray analysis were obtained by slow evaporation of a dichloroethane solution at ambient temperature. Crystal data: M=1648.17, space group $P\bar{1}$, a=19.826(6) Å, b=29.45(1) Å, c=12.234(4) Å, α=100.03(3)°, β= 100.26(2)°, γ=87.73(3)°, V=6922(9) Å^3, Z=4 and Dc=1.581 g cm^{-3}. Diffraction data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation using the ω-2θ scan mode to a maximun 2θ value of 45.1°. The structure was solved by Patterson method and refined to R=0.055 and R_W=0.062 for 487 parameters against 3843 (I>9σ(I)) out of 15579 unique reflections.

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(Received March 22, 1994)