CHEMISTRY LETTERS, pp. 1193-1196, 1979. Published by the Chemical Society of Japan

PERCHLORATE, TETRAFLUOROBORATE, AND HEXAFLUOROPHOSPHATE AS BRIDGING AND UNIDENTATE LIGANDS IN SOME PALLADIUM(II) COMPLEXES

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Dinuclear complexes $[PdX(R)(PPh_3)]_2$ (R = 2-(6-chloropyridyl)) containing ClO_4^-, BF_4^-, and PF_6^- as bridging ligands (X) have been prepared and characterized. Reactions with pyridine convert these anions into the unidentate ligands, giving rise to the $[PdX(R)(py)(PPh_3)]$ complexes which are more stable than the corresponding salts $[Pd(R)(py)_2(PPh_3)]X$.

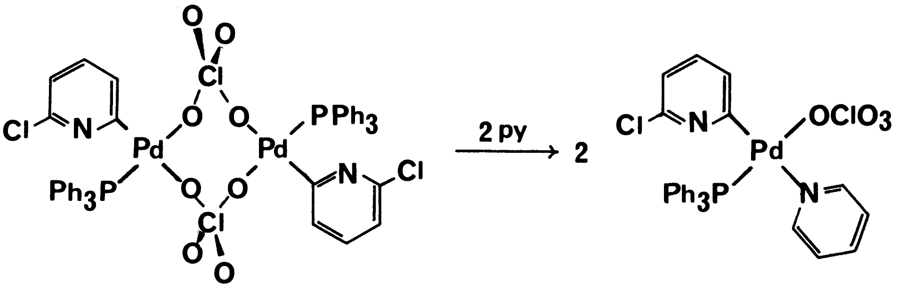
Perchlorate, tetrafluoroborate, and hexafluorophosphate are usually involved as counter anions in many metal complexes because of their poor ligating abilities. In fact, though the examples of metal complexes containing perchlorate as a ligand are steadily increasing,$^{1)}$ only a few tetrafluoroborato complexes$^{2)}$ and no hexafluorophosphato complex$^{3)}$ have been characterized so far. This communication reports some palladium(II) complexes containing these anions as bridging as well as unidentate ligands.

The Parent Complex $[PdCl(R)(PPh_3)_2]$ (R = 2-(6-chloropyridyl)), 1: Tetrakis(triphenylphosphine)palladium(0) (4.21 g) was allowed to react with a ten times excess (5.38 g) of 2,6-dichloropyridine in toluene (50 ml) at 90°C for 10 h under a nitrogen atmosphere and the mixture was left in a refrigerator for one day to deposit white crystals of 1 (2.68 g) in a 95% yield. Found: C, 63.18; H, 4.24; N, 1.80%; mol wt, 782 in CH_2Cl_2. Calcd for $C_{41}H_{33}NP_2Cl_2Pd$: C, 63.22; H, 4.27; N, 1.80%; mol wt, 779.

Synthesis and Characterization of $[PdClO_4(R)(PPh_3)]_2$, 2: Complex 1 (0.47 g) was dissolved in dichloromethane (15 ml) and benzene was added to make a 40 ml solution, to which under agitation was added dropwise a methanol solution (5 ml) of 1.5 times molar silver perchlorate (0.20 g). After stirring for 2 h, silver chloride was filtered off and the filtrate was concentrated to 15 ml to deposit a yellow precipitate (0.28 g) in an 80% yield. Found: C, 47.85; H, 3.34; N, 2.36%; mol wt, 1119 in CH_2Cl_2. Calcd for $C_{46}H_{36}N_2P_2O_8Cl_4Pd_2$: C, 47.57; H, 3.12; N, 2.41%; mol wt, 1161.

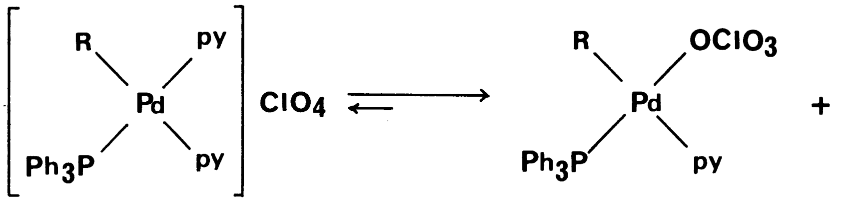
Complex 2 is air-stable and its dimeric structure is supported by the analytical and molecular weight data. IR spectra show three very strong peaks at 1174, 1150, and 1017 cm^{-1} as well as three medium bands at 640, 620 and 610 cm^{-1}, indicating the bidentate C_{2v} structure of the perchlorate ligand.[4] To our knowledge this is the first example of the dinuclear metal complex in which two perchlorate anions are connecting two metal atoms,[5] although the unsymmetrical single-bridging of this ion has been exemplified by $[CuClO_4(bpy)_2]ClO_4$.[6]

Complex 2 readily reacted with twice molar pyridine in dichloromethane at ambient temperature to give a mononuclear complex $[PdClO_4(R)(py)(PPh_3)]$, 3 in a 62% yield. Mol wt, 632 in CH_2Cl_2 (calcd 660). The bridge-splitting reaction gave rise to a single product with no sign of contamination by other geometrical isomers. Thus the $^{15}N\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 of complex 3* (3 containing labeled pyridine), which was prepared with ^{15}N-enriched (ca. 50%) pyridine, showed a single peak at -129.89 ppm (up field from external $NH_4{}^{15}NO_3$) and at 24.29 ppm (down field from external H_3PO_4), respectively. The small value of $^2J(P-N) = 3 \pm 1.5$ Hz strongly suggests that the pyridine occupies the site cis to the phosphine.[7]



2 3

The cationic complex 4 was isolated from the reaction of excess pyridine with 2 or 3 in a 71% yield, but is not stable in CH_2Cl_2 solution and the NMR studies revealed that the equilibrium (1) is favorable to 3.



(1)

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Synthesis and Characterization of $[PdBF_4(R)(PPh_3)]_2$, 5 and $[PdPF_6(R)(PPh_3)]_2$, 6: The reactions of 1 with silver tetrafluoroborate and silver hexafluorophosphate to prepare 5 and 6, respectively, were carried out in a similar fashion as the case of 2 except employment of a nitrogen atmosphere to prevent moisture. Compounds 5 and 6 were obtained in 65 and 60% yields, respectively. Found for 5: C, 47.48; H, 3.30; N, 2.35%; mol wt, 970 in CH_2Cl_2. Calcd for

$C_{46}H_{36}N_2P_2B_2F_8Cl_2Pd_2$: C, 48.63; H, 3.19; N, 2.47%; mol wt, 1136. Found for 6: C, 44.27; H, 3.20; N, 2.19%; mol wt, 1047 in CH_2Cl_2. Calcd for $C_{46}H_{36}N_2P_4F_{12}Cl_2Pd_2$: C, 44.12; H, 2.90; N, 2.24%; mol wt, 1252.

Bridge-splitting reactions of 5 and 6 with pyridine and 4-methylpyridine gave the mononuclear complexes $[PdBF_4(R)(py)(PPh_3)]$, 7 and $[PdPF_6(R)(pic)(PPh_3)]$, 8 in 65 and 68% yields, respectively. Mol wt: 7, 655 (calcd 647); 8, 837 (calcd 719) in CH_2Cl_2. The cationic complex $[Pd(R)(py)_2(PPh_3)]BF_4$, 9 was obtained by the reaction of 5 or 7 with a large excess of pyridine, but the corresponding hexafluorophosphate salt could not be isolated as a pure solid. It is quite interesting to note that perchlorate, tetrafluoroborate and hexafluorophosphate anions have a strong tendency (increasing in this order) of replacing the pyridine to occupy the coordination site in these complexes. The soft pyridyl and phosphine ligands might exert the antisymbiotic effect,8) making palladium(II) prefer a harder ligand X to pyridine.

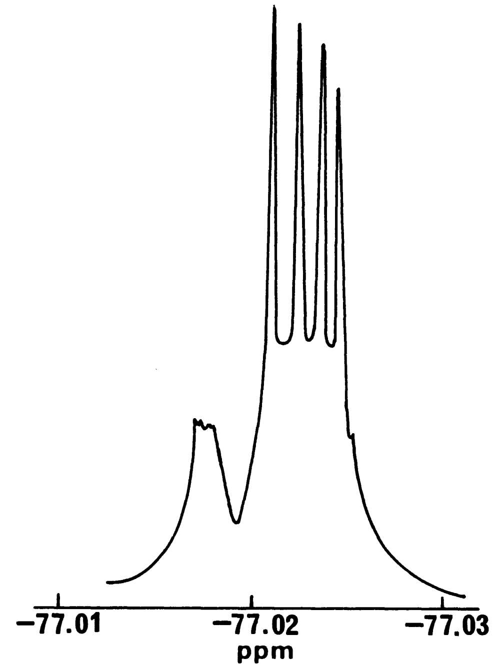
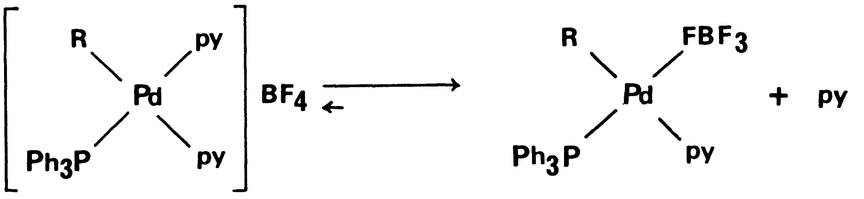


Fig. 1. ^{19}F NMR spectrum of 2-(6-chloropyridyl)(pyridine)tetrafluoroborato(triphenylphosphine)palladium(II) (7) in CD_2Cl_2 at 94 MHz with CF_3COOH as an external reference.

Infrared spectra of tetrafluoroborate and hexafluorophosphate anions become much complicated on ligation, but are not useful for distinguishing the linkage modes. The ^{19}F NMR spectrum of 5 measured in CD_2Cl_2 with a JEOL PS-100 spectrometer shows a broad signal at -76.17 ppm9) without discriminating the two kinds of fluorine atoms. As is seen in Fig. 1, on the other hand, the spectrum of the mononuclear complex 7 exhibits two kinds of signals at about -77.02 ppm. The intensity ratio of 3:1 seems to indicate that the quartet signal in the higher field may be assigned to the three uncoordinated fluorine atoms and the complicated lower field one to the coordinated fluorine atom. The spectrum of 9 is quite similar to that of 7, two signals appearing at about -77.45 ppm. The equilibrium (2) seems to be almost completely shifted to right in this solution. In fact addition of pyridine in excess



(2)

9 7

to the solution of 7 in CD_2Cl_2 did not change the pattern of spectrum shown in Fig. 1, but shifted the whole spectrum up to -77.45 ppm.

The ^{19}F NMR spectrum of 6 is composed of a broad doublet at 5.93 ppm with $^{1}J(P-F) = 712.5$ Hz. The fluorine atoms in 8 also resonate at 5.74 ppm as a doublet with $^{1}J(P-F) = 706.9$ Hz. The spectral patterns for these complexes are quite similar to each other, suggesting existence of some kind of dynamic process in dichloromethane. On addition of excess pyridine to a solution of 6 or 8 a sharp doublet is observed at 5.83 ppm which $^{1}J(P-F) = 704$ Hz, which might be a signal of $[Pd(R)(py)_2(PPh_3)]PF_6$. Potassium hexafluorophosphate in aqueous solution was reported to show a doublet at 7.7 ppm with $^{1}J(P-F) = 706$ Hz.[10)]

The authors wish to express their hearty thanks to Mr. Junichi Gohda for elemental analyses, to Mr. Kiyoshi Kida of Tokushima University for ^{19}F NMR measurements, and to Mr. Tetsu Hinomoto of JEOL, Ltd. for ^{15}N and ^{31}P NMR measurements. Thanks are also due to the Ministry of Education for Grant-in-Aid for Special Project Research (No. 311706).

References and Notes

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(Received August 2, 1979)