Syntheses and Characterization of Palladium and Platinum Complexes of Phosphorin

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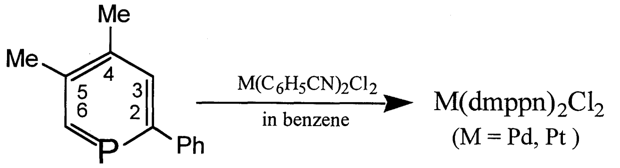
Palladium and Platinum complexes of 4,5-dimethyl-2-phenylphosphorin (dmppn) were synthesized through ligand exchange reactions with $M(C_6H_5CN)_2Cl_2$ (M = Pd, Pt). It was confirmed by means of ^{31}P- and ^{13}C-NMR spectroscopy that these complexes effect strong π-back donation from metal to phosphorin and have a square planar structure with *cis* configuration in dichloromethane solution.

The tertiary phosphine complexes of palladium and platinum have been well documented. It is particularly interested that these complexes demonstrate catalytic properties such as the hydrogenation of alkenes.[1] In the previous communication[2] we reported that the phosphorin coordinates to copper(I) through phosphorus donor atom that is included in a conjugate π-system and that the phosphorus atom in the phosphorin has a character of strong π-acceptor compared with that in phosphines. This character of the phosphorin ligand can afford an approach to create new catalytic functions in palladium and platinum complexes of the phosphorin. We report herein the syntheses of the palladium(II) and platinum(II) complexes of 4,5-dimethyl-2-phenylphosphorin (dmppn)[3] and their characterization by means of NMR spectroscopy. These two complexes are the first example for the palladium(II) and platinum(II) phosphorin complexes that are isolated and well characterized.



dmppn

Attempts to obtain the palladium and platinum complexes through direct reactions of MCl_2 (M = Pd, Pt) with dmppn in methanol were unsuccessful. Thus, $Pd(dmppn)_2Cl_2$ (**1**)[4] and $Pt(dmppn)_2Cl_2$ (**2**)[5] were synthesized through the ligand-exchange reaction of $M(C_6H_5CN)_2Cl_2$ (M = Pd, Pt) by dmppn in benzene solution. The complex **1** precipitated as orange compound and the complex **2** was deposited upon addition of hexane as pale yellow compound. Two complexes were isolated as air stable ones, but reacted with moisture and methanol in solution.

In the ^{31}P-NMR spectra (160 MHz), the complex **1** showed a resonance at 151.3 ppm while **2** at 134.3 ppm. These observations clearly demonstrate that the phosphorin coordinate to Palladium(II) and Platinum(II) through a lone-pair (η^1-type coordination) of the phosphorus atom.[6] It is noticeable that **1** and **2** showed significant upfield shifts of the phosphorus resonance by 32.5 and 49.6 ppm, respectively, relative to that of the free dmppn as shown in Table 1. The degree of the upfield shift in complex **2** was greater than that of **1**. Such coordination shifts were reported in previous studies.[7] The coordination shifts in palladium and platinum complexes of phosphines and phosphites were correlated with the chemical shifts of the free ligands[8] and may be interpreted using three contributions: the electronegativity of substituents, bond angles, and π-bonding character of substituents. The coordination shifts that were observed in present study appear to fall coincidence with above trend. However the chemical shifts of adjacent carbon atoms to phosphorus (C2 and C6) also showed upfield shifts in the range of 13-17 ppm and those of C3 and C5 did downfield shifts in the range of 3-7 ppm as shown in Table 1. These changes in the direction of the shifts indicate the alteration of π-system of the phosphorin due to π-back donation. Main factor of these upfield shifts in the phosphorin is plausibly attributed to π-back donation from a metal center to stabilize the metal-phosphorus bonding. The character of π-acceptor in the phosphorin was suggested by Elischenbroich *et al.*[9]

Table 1. ^{31}P- and ^{13}C-NMR data for free ligand, $Pd(dmppn)_2Cl_2$ **1** and $Pt(dmppn)_2Cl_2$ **2** in CD_2Cl_2 at 25 °C

sample	$\delta^{31}P^a$ $(\Delta\delta)^c$	$\delta^{13}C^b$ $(\Delta\delta)^c$				
		C2	C6	C3	C5	C4
dmppn	183.8	168.5	154.8	136.1	142.0	139.5
1	151.3 (32.5)	155.3 (13.2)	141.3 (13.6)	139.0 (-2.9)	149.2 (-7.2)	138.5 (1.0)
2	134.3 (49.6)	151.1 (17.4)	137.0 (17.8)	139.8 (-3.7)	149.0 (-7.0)	139.1 (0.4)

^{a}Chemical shifts in ppm relative to H_3PO_4 (85% aqueous solution). ^{b}Chemical shifts in ppm relative to TMS. $^c\Delta\delta = \delta$(free dmppn) - δ(complex).

The ^{31}P-NMR spectrum of platinum complex **2** is most informative for the determination of *cis* and *trans* configurations in the solution. The coupling constants J (^{31}P-^{195}Pt) for $Pt(PR_3)_2Cl_2$ (PR_3 = tertiary phosphines) are generally greater than 3000 Hz in the case of *cis* configuration of two phosphorus atoms and around 2000 Hz in the case of *trans* configuration.[10] It was reported by Schmid *et al*[6] that the cyclic phosphine complex of platinum showed J (^{31}P-^{195}Pt) of 4156 Hz and two phosphorus atoms occupied mutually *cis* position as determined by X-ray crystallography. The coupling constants J (^{31}P-^{195}Pt) for **2** was determined to be 4052 Hz. This value supports that the complex **2** has the *cis* configuration in $CDCl_3$ solution (Figure 1).

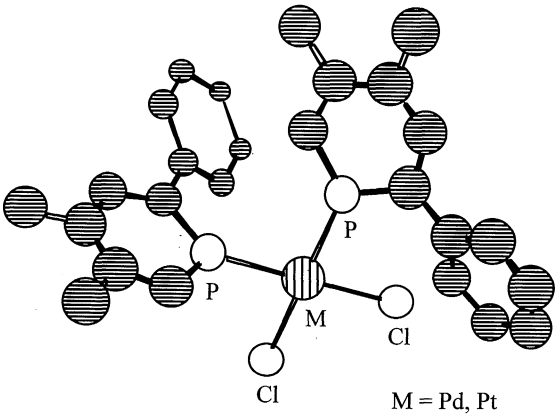


Figure 1. The proposed structure of **1** and **2**.

The phosphorus resonance of palladium complex **1** was observed as a slightly broad singlet (half-line width 49 Hz). The *trans* isomers of bis(*tert*-phosphine)palladium(II) complexes, *trans*-$Pd(PR_3)_2Cl_2$, have greater coupling constants J(^{31}P-^{31}P) than 150 Hz while the *cis* isomers have smaller ones than 20 Hz.[11] On the other hand, the ^{13}C signals attributable to the carbons adjacent to the phosphorus were observed as two doublets : at 137.0 (J = 57 Hz) for C2 and 151.1 ppm (J = 51 Hz) for C6. In the ^{13}C-NMR spectra of $Pd(PR_3)_2Cl_2$, the *cis* and *trans* isomers show distinct multiplicities : For the *cis* isomers, the ^{13}C resonances for the carbons adjacent to the phosphorus have been observed as five-line multiplets, non-1:2:1 triplets, doublets of doublets, or doublets ; for the *trans* isomers, those resonances have appeared as 1:2:1 triplets in many cases studied thus far.[10] These observations suggest that the complex **1** also possesses *cis* configuration in CD_2Cl_2 solution as shown in Figure 1.

References and Notes

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4 **1·benzene**, Found: C, 58.60; H, 4.92%; Anal. Calcd for $C_{32}H_{32}Cl_2P_2Pd$: C, 58.68 H, 4.96%. Yield 83%.

5 **2·benzene**, Found: C, 51.12; H, 4.35%; Anal. Calcd for $C_{32}H_{32}Cl_2P_2Pt$: C, 51.62.H, 4.34%. Yield 75%.

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12 NMR data for complex **1**: ^{1}H-NMR ($CDCl_3$, TMS) 7.641 (d, J=17 Hz, 1H, 6-H), 7.465 (d, J=27 Hz, 1H, 3-H), 7.20-7.57 (m, 5H, Ph-H), 2.275 (d, J=8 Hz, 6H, 4-Me) 2.266 (s, 3H, 5-Me); ^{13}C-NMR (CD_2Cl_2, TMS) 138.95 (t, J=11 Hz, 3- C), 138.52 (t, J=20 Hz, 4- C), 149.15 (t, J=28 Hz, 5- C), 141.24 (d, J=34 Hz, 6- C), 155.33 (d, J=43 Hz, 2- C); ^{31}P-NMR ($CDCl_3$, 85% H_3PO_4) 151.3 (s).

13 NMR data for complex **2**: ^{1}H-NMR ($CDCl_3$, TMS) 7.504 (d, J=23 Hz, 1H, 6-H), 7.530 (d, J=11 Hz, 1H, 3-H), 7.20-7.57 (m, 5H, Ph-H), 2.250 (d, J=7 Hz, 3H, 4-Me), 2.297 (s, 3H, 5-Me); ^{13}C-NMR (CD_2Cl_2, TMS) 139.84 (t, J=10 Hz, 3- C), 139.11 (t, J=9 Hz, 4- C), 149.00 (t, J=18 Hz, 5- C), 137.04 (d, J=51 Hz, 6- C), 151.07 (d, J=57 Hz, 2- C); ^{31}P-NMR ($CDCl_3$, 85% H_3PO_4) 134.3 (d, J(Pt-P) = 4052 Hz).