Platinum Complexes of Phospholes with Reduced Pyramidal Character from Steric Crowding

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Introduction

During the last two decades a huge number of phosphorus-containing ligands have been synthesized and tested in various homogeneous catalytic reactions.[1] A large part of these research efforts in the field of asymmetric catalysis has been aimed at exploiting the potential of phosphole-core ligands. Both dibenzophospholyl[2−5] and binaphthophospholyl[6,7] moieties were connected to chiral carbon backbones in chelating ligands, which were used in enantioselective platinum-catalyzed hydroformylation. The coordination chemistry of diphosphines and diphospholes with platinum proved to be remarkably different.[3,6] Despite the small pK_a values of phospholes compared with phosphines, it has been shown that both types of ligands investigated to date coordinate to various transition metals in a similar manner.[8,9]

However, the reaction of the sterically crowded 1-arylphospholes [1-(2′,4′,6′-triisopropylphenyl)-3-methylphosphole (**1**),[10] 1-(2′,4′,6′-tri-*tert*-butyl-phenyl)-3-methylphosphole (**2**),[11] and 1-(2′,4′-di-*tert*-butyl-6′-methylphenyl)-3-methylphosphole (**3**);[12] Figure 1] with $PtCl_2(PhCN)_2$ shows some novel peculiarities. All three ligands possess a relatively large Bird index,[13] reflecting an increased aromatic character.

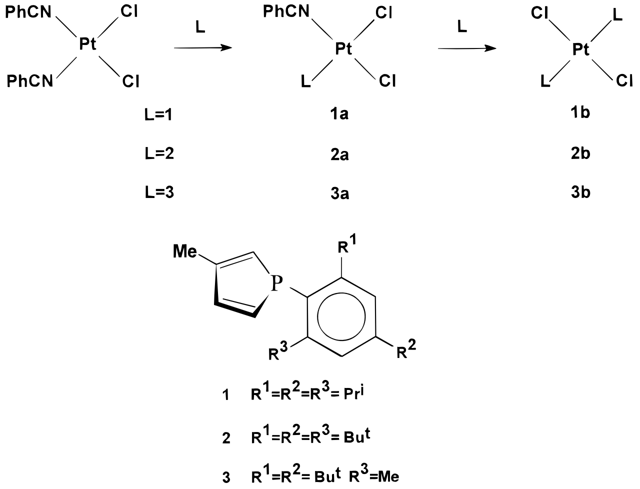

Figure 1.

Table 1. ^{31}P NMR Data of Platinum Complexes Containing Phosphole Ligands **1**, **2**, **3**, and **4**[a]

complexes		$\delta^{31}P$ [ppm]	$^1J(^{195}Pt,^{31}P)$ [Hz]
cis-$PtCl_2$(**1**)(PhCN)	(**1a**)	5.0	3160
trans-$PtCl_2$(**1**)$_2$	(**1b**)	23.45	2347
	(**1b′**)	23.50	2347
cis-$PtCl_2$(**2**)(PhCN)	(**2a**)	9.0	3302
trans-$PtCl_2$(**2**)$_2$	(**2b**)	24.2	2494
	(**2b′**)	23.8	2490
cis-$PtCl_2$(**3**)(PhCN)	(**3a**)	9.5	3217
trans-$PtCl_2$(**3**)$_2$	(**3b**)	26.0	2390
cis-$PtCl_2$(**4**)$_2$		8.8	3350
trans-$PtCl_2$(**4**)$_2$		41.7	2029
trans-PtCl($SnCl_3$)(**4**)$_2$[b]		16.2	2156

[a] All spectra were measured in $CDCl_3$ at 121.4 MHz at 298 K. [b] $^2J(^{117,119}Sn,^{31}P)$ = 233 Hz (the ^{117}Sn and ^{119}Sn satellites coincide).

Results and Discussion

By reaction of **1** with $PtCl_2(PhCN)_2$ in $CDCl_3$ the immediate formation of cis-$PtCl_2$(L)(PhCN) (**1a**) possessing an unprecedented structure and two diastereomers of the *trans*-$PtCl_2$(**1**)$_2$ (**1b** and **1b′**) has been observed by NMR spectroscopy at room temperature. The sterically most congested ligand **2** did not react over a period of several days. However, both mono- and bisphosphole complexes of the above types were formed in 4 weeks.

The selective formation of **3a** was observed in the case of **3** a few minutes after the reaction started. After a week the substitution of the "second" benzonitrile ligand also occurred to yield **3b**. The $PtCl_2(PhCN)_2$ precursor was completely converted to the mixture of **3a** and **3b** in about 2 h, and no further substantial changes were observed, even after 38 days. Both complexes were isolated by stopping the reactions at different stages.

The phosphole ligand with the most pronounced basic character (1-phenyl-3,4-dimethylphosphole, **4**), which possesses the "most pyramidal" phosphorus in this phosphole ligand series (and was reacted as a comparison to the other phosphole ligands), behaves principally like monotertiary phosphines: its reaction with $PtCl_2(PhCN)_2$ under the same conditions gave the expected $PtCl_2$(**4**)$_2$ complexes (cis/trans = 97/3).[14] This mixture of complexes was converted quantitatively to *trans*-PtCl($SnCl_3$)(**4**)$_2$ upon addition of $SnCl_2$.[14]

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Table 2. ^{1}H NMR Data for Phosphole **3**[a] and for Its Platinum Complex **3a**

	3			**3a**		
	δ [ppm]	$J(^{31}P,^1H)$ [Hz]	$J(^1H,^1H)$ [Hz]	δ [ppm]	$J(^{31}P,^1H)$ [Hz]	$J(^1H,^1H)$ [Hz]
H-2	6.46	37.4	1.6; *ca.* 1.5	6.56	35	<2; <2
H-4	6.84	16.7	7.0; 1.6	6.70	13	
H-5	6.94	37.4	7.0; 2.4	6.98	35.5	<2
3-CH_3	2.24	6.0	*ca.* 1.5	2.13	<2	<2
8-CH_3	1.72	*ca.* 0.5	–	3.28	–	
H-9	6.94		2.3	6.93 (brs)		
10-$C(CH_3)_3$	1.28		–	1.24	–	
H-11	7.41	6.0	2.3	7.11	4.0	<2
12-$C(CH_3)_3$	1.73	*ca.* 2	–	1.48	–	
Ph(*o*)				6.84[b]		
Ph(*m*)				7.32[b]		
Ph(*p*)				7.59[b]		

[a] The numbering of protons is in agreement with that used in ref 12. [b] The chemical shifts of the corresponding Ph(*o*), Ph(*m*), Ph(*p*) protons in "free" PhCN and $PtCl_2(PhCN)_2$ are at 7.64, 7.46, 7.59 and 7.80, 7.55, 7.73 ppm, respectively.

The $^1J(^{195}Pt,^{31}P)$ coupling constants of 3160, 3302, and 3217 Hz, observed for **1a**, **2a**, and **3a**, respectively (Table 1), are characteristic of complexes having phosphorus and chloro ligands in trans disposition.[15] Although the *cis*-$PtCl_2(L)_2$ complexes are expected to give similar coupling constants, the coordination of one PhCN ligand is undoubtedly confirmed in all of the above cases (Table 2).[16]

It is worth noting that the slight differences in the $^1J(Pt,P)$ coupling constants for both the *cis*-$PtCl_2(L)(PhCN)$ and *trans*-$PtCl_2(L)_2$ (see below) complexes suggest that the platinum−phosphorus bond is weakened in the ligand order **2** > **3** > **1** > **4**, i.e., by decreasing ligand aromaticity.

The $^1J(^{195}Pt,^{31}P)$ coupling constants of about 2500 Hz are typical for *trans*-$PtCl_2$(tertiary phosphine)$_2$ complexes. In case of **3** the *cis*-$PtCl_2(\mathbf{3})(PhCN)$ complex reacts further with **3** to produce a *trans*-complex (**3b**). By using the other two ligands (**1** and **2**) a similar reaction sequence was assumed by the predominance of the *cis*-monophosphole complexes (**1a** and **2a**) during the whole reaction. The high selectivity toward *trans*-$PtCl_2(L)_2$ complexes can be explained by the formation of five-coordinate $PtCl_2(L)_2(PhCN)$ species (one of the L ligands is in the apical position), which undergoes rapid geometrical isomerization at the platinum center to *trans*-$PtCl_2(L)_2(PhCN)$ (PhCN is in apical position). The *trans*-$PtCl_2(L)_2$ product is formed by loss of PhCN.

It is worth noting that the *trans*-bis-monophosphole complexes with **1** and **2** gave two sets of signals of very similar ^{31}P NMR characteristics (**1b**, **1b′** and **2b**, **2b′**, respectively). This phenomenon can be explained by the loss of "flattening" of the aryl ring upon coordination of the phosphorus to platinum. Because the phosphole ring is "asymmetrically" substituted by a methyl substituent (3-CH_3), the coordinated phosphole of more pronounced pyramidal character possesses an sp^3 phosphorus stereogenic center. Therefore, the use of a racemic phosphole ligand results in a racemic (RR/SS) and a "meso" (RS) *trans*-$PtCl_2(L)_2$ complexes. The two *trans*-complexes obtained both in case of **1** and **2** are diastereomers, and consequently gave rise to slightly different NMR spectra.

The most striking difference between ^{1}H chemical shifts of coordinated and noncoordinated ligands has been observed in case of **3** (Table 2). The largest effect has been observed for the *ortho*-methyl substituent of the aryl ring upon complexation. The highly shielded singlet at 1.72 ppm has been shifted to 3.28 and 3.15 ppm in **3a** and **3b**, respectively. In the same time, the *ortho*-*tert*-butyl substituent of the aryl ring was shifted from 1.73 ppm to 1.48 and 1.38 ppm in **3a** and **3b**, respectively. The above deshielding effect on the methyl group and the loss of the deshielding effect in case of the *ortho*-*tert*-butyl group are accompanied by the decrease of $^4J(^{31}P,^1H)$ coupling constants of the C-3 methyl substituent of the phosphole ring and by that of the *meta*-protons of the aryl ring.

The decrease of the $J(^{31}P,^1H)$ coupling constants refers to the pyramidal arrangement of the substituents of the coordinated phosphorus, i.e. the smaller effect of the phosphorus lone-pair on $J(P,H)$ coupling constants for protons of the phosphole ring and for *meta*-protons of the aryl ring. The surprisingly high deshielding effect on the *ortho*-methyl substituent can be explained by its position under the phosphole ring (in the deshielding segment of the phosphole moiety) which is due to the loss of perpendicular arrangement of phosphole and aryl rings upon coordination.

Experimental Section

Chemicals. The 1-arylphosphole ligands (**1**, **2**, and **3**) were synthesized as described earlier.[10−12] Platinum(II) chloride was purchased from Aldrich. Benzene was distilled under argon from sodium in the presence of benzophenone.

The $PtCl_2(PhCN)_2$ precursor was prepared as described previously.[17] The $PtCl_2(L_2)$ complexes were prepared in refluxing benzene by the widely used "benzonitrile method".[17]

Instrumentation. ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer at 300 and 121.4 MHz, respectively. Chemical shifts are reported in δ ppm, referred to TMS (tetramethylsilane) as internal standard and to orthophosphoric acid (85%, higher fields refer to lower chemical shifts) as external standard.

All experiments were carried out under an argon atmosphere by using standard inert Schlenk techniques.

Preparation of $PtCl_2(L)_2$ (L = 1 or 3). In a typical experiment, a 0.1 mmol amount of $PtCl_2(PhCN)_2$ was dissolved in 8 mL of refluxing benzene and a solution of 0.1 mmol of **1** (or **3**) in 4 mL of benzene was added. The experiment was conducted for 6 h. A pale yellow solid was formed, which was filtered off after the mixture was cooled to room temperature. The product was recrystallized from benzene.

Characterization of Isolated Platinum Complexes. $PtCl_2(1)_2$. ^{31}P NMR: See Table 1. Anal. Calcd for $C_{40}H_{58}P_2Cl_2Pt$ (M = 866.83): C, 55.42; H, 6.74; Cl, 8.18. Found: C, 55.77; H, 6.91; Cl, 7.93; yield, 32%.

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$PtCl_2(3)(PhCN)$. ^{31}P NMR: See Table 1. Anal. calcd for $C_{27}H_{34}NPCl_2Pt$ ($M = 669.53$): C, 48.44; H, 5.12; N, 2.09; Cl, 10.59. Found: C, 48.67; H, 5.04; N, 2.41; Cl, 9.88; yield, 27%.

$PtCl_2(3)_2$. ^{31}P NMR: See Table 1. Anal. calcd for $C_{40}H_{58}P_2Cl_2Pt$ ($M = 866.83$): C, 55.42; H, 6.74; Cl, 8.18. Found: C, 55.70; H, 6.95; Cl, 7.86; yield, 45%.

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