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Coordination chemistry and hydroformylation activity of platinum complexes containing 1-aryl-phospholes

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

Abstract

The reaction of the sterically crowded 1-aryl-phospholes (1-(2′,4′,6′-tri-isopropylphenyl)-3-methylphosphole (**1**), 1-(2′,4′,6′-tri-*tert*-butylphenyl)-3-methyl-phosphole (**2**) and 1-(2′,4′-di-*tert*-butyl-6′-methylphenyl)-3-methylphosphole (**3**)) with $PtCl_2(PhCN)_2$ was investigated by NMR spectroscopy. Significant differences in their reactivity towards $PtCl_2(PhCN)_2$ have been observed. Both *cis*-$PtCl_2$(phosphole)(PhCN) and *trans*-$PtCl_2$(phosphole)$_2$ complexes were formed under normal reaction conditions. The corresponding reaction with the more basic 1-phenyl-3,4-dimethyl-phosphole (**4**) resulted in the immediate formation of *cis*-$PtCl_2$(**4**)$_2$ as the major product accompanied by $\approx 3\%$ *trans*-$PtCl_2$(**4**)$_2$. The structure of the two types of platinum complexes in solution has been confirmed by $^1J(^{195}Pt,^{31}P)$ coupling constants in ^{31}P-NMR and several shielding effects in ^{1}H-NMR spectrometry. The reduced aromatic character of the coordinated phosphole ligands has been confirmed by the pyramidalization of the phosphorus and the loss of the perpendicular arrangement of the phosphole and aryl rings. While the reaction of the sterically congested phospholes (**1**, **2**) with $[Rh(nbd)Cl]_2$ resulted in the formation of Rh(nbd)(phosphole)Cl complexes, the most basic **4** brought about the $[Rh(nbd)(\mathbf{4})_2]^+$ cation. Both the conversion and the regioselectivity of platinum- and rhodium-catalysed hydroformylation of styrene show strong dependence on the basicity of the phosphole ligand.

Keywords: Platinum; Phosphole; NMR; Hydroformylation; Steric congestion

1. Introduction

Besides the transition metal complexes of optically active ditertiary phosphines, those of chelating diphospholes are of increasing importance in asymmetric catalysis [1–4]. The optically active chelating ligands containing both dibenzophospholyl [5–8] and binaphthophospholyl [9–11] moieties have been used successfully in asymmetric carbonylation reactions, among them enantioselective platinum-catalysed hydroformylation. Although the coordination of analogous diphosphines and diphospholes to platinum(II) is remarkably different [9,12], monophosphines and simple monophospholes possessing basically pyramidal phosphorus donor atoms show similar behaviour [13,14].

In the present work the coordination chemistry of various sterically congested P-aryl-phospholes of a novel type towards platinum is described. The effect of the 2,4,6-substituents of the aryl ring on the ligand reactivity, product selectivity and type of coordination, as well as the carbonylation activity of some of these platinum–phosphole systems will be discussed.

2. Results and discussion

2.1. The reaction of phosphole ligands (*1*, *2*, *3* and *4*) with $PtCl_2(PhCN)_2$

In spite of the considerable lone-pair delocalization within the phosphole ring, and as a consequence of

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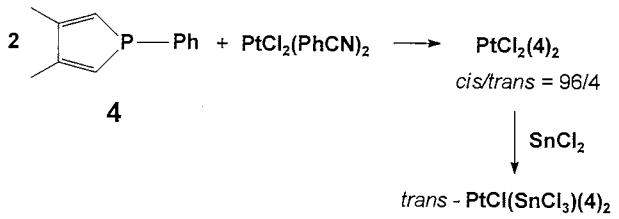


Fig. 1. Reaction of **4** [16] with $PtCl_2(PhCN)_2$.

that, the relatively large Bird index [15] and small pK_a values compared with phosphines, it has been shown that the coordination chemistry of monophospholes investigated to date is very similar to that of much more basic monotertiary phosphines.

For example, the well-known 1-phenyl-3,4-dimethylphosphole (**4**) has the most pronounced basic character (possesses the 'most pyramidal' phosphorus) of the monophospholes investigated in this study. It behaves principally like monotertiary phosphines: its reaction with $PtCl_2(PhCN)_2$ gave the expected mixture of *cis*- and *trans*-$PtCl_2(\mathbf{4})_2$ complexes, which was converted quantitatively to *trans*-$PtCl(SnCl_3)(\mathbf{4})_2$ upon addition of $SnCl_2$ as has been found earlier (Fig. 1, [16]).

However, the phospholes of reduced pyramidal character from steric crowding (**1** [17], **2** [18], **3** [19]) due to the steric congestion of the *ortho*-substituents of the phenyl ring with the atoms of the phosphole ring, show a significant difference in reactivity towards $PtCl_2(PhCN)_2$ (Fig. 2, Table 1).

By allowing **1** to react with $PtCl_2(PhCN)_2$ in $CDCl_3$, the immediate formation of **1a** possessing unprecedented structure and two diastereomers of the *trans*-

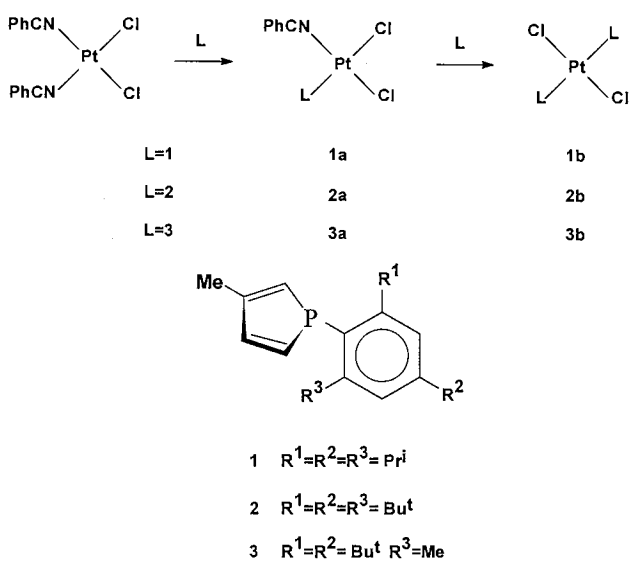


Fig. 2. Reaction of sterically congested phospholes (**1–3**) with $PtCl_2(PhCN)_2$.

Table 1
Ratio of *cis*-$PtCl_2(L)(PhCN)$/*trans*-$PtCl_2(L)_2$ (**a**/**b**) in the reaction of $PtCl_2(PhCN)_2 + 2L$ (L = monodentate phosphole ligand)[a]

L	Reaction time	a	b
1	0.5 h	78	22
	1 h	49	51
	170 h	45	55
2	0.5 h	–	–
	28 days	62	38[b]
3	0.5 h	100	0[c]
	7 days	88	12
	38 days	83	17

[a] The ratios and the composition of the reaction mixtures are determined by ^{31}P-NMR.

[b] Due to oxidation of **2** and its consecutive dimerization 23% of the total phosphorus is in the form of **2′**.

[c] **3b** can be found in the reaction mixture only in traces (less than 0.5%).

$PtCl_2(\mathbf{1})_2$ (**1b** and **1b′**) showing very similar NMR characteristics has been observed.

The use of the sterically most congested ligand **2** resulted in mono- and bis-phosphole complexes in long reaction times, only (Table 1). The highly unreactive feature of this ligand was also shown by the fact, that in spite of the ligand excess, some unreacted **2** (5%) and, as a consequence of the $\mathbf{2}/PtCl_2(PhCN)_2 = 2/1$ ratio, also some unreacted platinum precursor ($PtCl_2(PhCN)_2$) were detected even after 1 month.

It is worth noting that cyclodimerization of the primarily formed phosphole oxide took place to a great extent during this prolonged reaction. The characteristic pair of doublets in the ^{31}P-NMR spectrum (AX spin system; 59.0 and 85.0 ppm, $^3J(^{31}P,^{31}P) = 40$ Hz) has been assigned to the Diels–Alder cycloadduct, **2′** (Fig. 3). In accordance with earlier findings, the monomeric phosphole oxide could not be detected due to its fast dimerization.

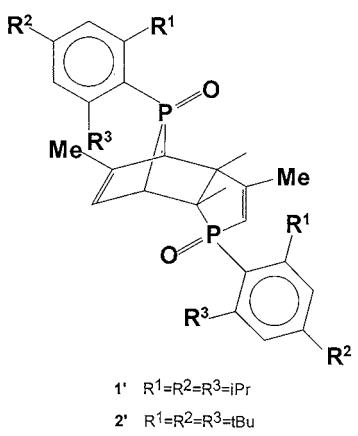


Fig. 3. The dimers of phosphole oxides of **1** and **2**.

Table 2
^{31}P-NMR data of Pt complexes containing phosphole ligands, **1, 2, 3** and **4**[a]

Complexes		δP (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).

The monophosphole–platinum complex **(3a)** was formed selectively in a few minutes after starting the reaction, when **3** was used as the sterically congested monophosphole. Although the substitution of both benzonitrile ligands also took place in part in a consecutive reaction yielding **3b**, the mixture of **3a** and **3b** was formed in a few hours. The selective formation of **3b** by complete substitution has not been achieved even under long reaction times.

2.2. NMR characterisation of platinum–phosphole complexes

(i) The reaction of **1**, **2** and **3** with $PtCl_2(PhCN)_2$ resulted in platinum complexes possessing $^1J(^{195}Pt,^{31}P)$ coupling constants of 3160, 3302 and 3217 Hz (Table 2). These coupling constants are of diagnostic value for a P–Pt–Cl *trans* arrangement and similar values have been obtained for a number of *cis*-$PtCl_2(P)_2$-type complexes [20]. However, in the case of **1a**, **2a** and **3a**, the coordination of a benzonitrile ligand is unambiguously confirmed by NMR (Table 3). Therefore, the coordination of only one phosphole ligand is shown in the primary products, the rather unexpected *cis*-$PtCl_2$(L)(PhCN) type complexes. In the case of a two-fold excess of **3,** it was clearly demonstrated that a single product (**3a**) was formed, half of the ligand remained unreacted and the total amount of $PtCl_2(PhCN)_2$ was consumed.

However, in the case of **4**, on the basis of ^{1}H-NMR evidence (no traces of coordinated benzonitrile), the ^1J(Pt,P) coupling constants of 3350 and 2029 Hz are assigned unambiguously to *cis*- and *trans*-$PtCl_2$(**4**)$_2$, respectively.

(ii) The $^1J(^{195}Pt,^{31}P)$ coupling constants of about 2500 Hz are typical for phosphorus donors *trans* to a phosphorus ligand and are of diagnostic value. In the case of **3** it was shown that the *cis*-$PtCl_2$(**3**)(PhCN) complex formed primarily reacts further with **3**, resulting in the *trans*-complex (**3b**). A similar reaction sequence was assumed for the other two ligands (**1** and **2**). The *cis*-monophosphole-complexes (**1a** and **2a**) and the corresponding *trans*-diphosphole complexes (**1b** and **2b**) are present in similar amounts at the end of the reaction when no further changes were detected (Table 1).

The bis-monophosphole complexes containing **1** and **2** gave two sets of signals of very similar ^{31}P-NMR characteristics assigned to **1b**, **1b′** and **2b**, **2b′**, respectively. This phenomenon can be explained by the presence of an sp^3 phosphorus stereogenic centre upon coordination resulting in the formation of racemic (*R*,*R*/*S*,*S*) and 'meso' (*R*,*S*) *trans*-$PtCl_2(L)_2$ complexes. It must be noted that the nearly 1/1 diastereomeric

Table 3
^{1}H-NMR data for phosphole **3** and for its platinum-complexes, **3a** and **3b**

	3			**3a**[a]		**3b**[a]		**$PtCl_2$(PhCN)$_2$**
	δ (ppm)	$J(^{31}P,^1H)$ (Hz)	$J(^1H,^1H)$ (Hz)	δ (ppm)	$J(^{31}P,^1H)$ (Hz)	δ (ppm)	$J(^{31}P,^1H)$ (Hz)	δ (ppm)
H-2	6.46	37.4	1.6; ca. 1.5	6.56	35	6.51	ca. 34	–
H-4	6.84	16.7	7.0; 1.6	6.70		[b]		–
H-5	6.94	37.4	7.0; 2.4	6.98		[b]		–
3-CH_3	2.24	6.0	ca. 1.5	2.13	<2	2.09		–
8-CH_3	1.72	ca. 0.5	–	3.28	–	3.15	–	–
H-9	6.94		2.3	6.93 (brs)		[b]		–
10-C(CH_3)$_3$	1.28		–	1.24	–	1.23	–	–
H-11	7.41	6.0	2.3	7.11	ca. 4	[b]		–
12-C(CH_3)$_3$	1.73	ca. 2	–	1.48	–	1.38	–	–
Ph(*o*)				6.84[c]				7.80
Ph(*m*)				7.32[c]				7.55
Ph(*p*)				7.59[c]				7.73

[a] All the $J(^1H,^1H)$ values are smaller than 1.5 Hz in **3a** and **3b**.
[b] The multiplets of the complex overlap with those of the non-coordinating ligand.
[c] The chemical shifts of the corresponding Ph(*o*), Ph(*m*), Ph(*p*) protons in 'free' PhCN are at 7.64, 7.46, 7.59.

ratio of **1b**/**1b**′ determined on the 'in situ' mixture by NMR measurements was shifted to approximately 2/1 when the reaction of **1** with $PtCl_2(PhCN)_2$ was carried out in benzene (See Section 3) and crystallised from the reaction mixture. This phenomenon can be explained both by solvent effects on the substitution of the second benzonitrile ligand and by the different solubilities of the diastereomers.

(iii) The change of the shielding effect on some protons of both the phosphole and the benzonitrile ligands proved to be extremely useful from the point of view of structural characterization. The largest effects have been observed in **3a** and **3b** (Table 3). (The numbering of the phosphole positions is the same as described earlier [19].) The largest effects have been observed for 8-CH_3 (*ortho* methyl substituent of the aryl ring) and 12-$C(CH_3)_3$ group (*ortho tert*-butyl substituent of the aryl ring) both in **3a** and **3b**. The deshielding effect on 8-CH_3 and the loss of the deshielding effect in the case of the ortho *tert*-butyl group are accompanied by a decrease in the magnitude of $J(^{31}P,^{1}H)$ coupling constants to the C-3 methyl substituent of the phosphole ring and to H-11 (one of the *meta* protons of the aryl ring).

On the basis of the changing of the shielding effects and the decrease of the J(P,H) coupling constants (Table 3), both the change of the nearly planar character of the phosphorus towards a pyramidal one and the loss of perpendicular arrangement of phosphole and aryl rings upon coordination can be envisaged.

2.3. NMR characterisation of rhodium–phosphole complexes

The most aromatic phosphole (**2**) reacted slowly with $[Rh(nbd)Cl]_2$ in $CDCl_3$ and Rh(nbd)(**2**)Cl (**2c**) (δ, 30.8 ppm, $^{1}J(Rh–P) = 125$ Hz) was formed with $\approx 13\%$ conversion. Upon prolonged reaction (more than 10 days) the characteristic pair of doublets assigned to the cyclodimerization product of the phosphole oxide (**2**′, Fig. 3) was detected but no further reaction towards **2c** was observed. Surprisingly, no formation of Rh–phosphole complexes has taken place even in traces when $Rh(CO)_2(acac)$ complex was used as starting material.

The reaction of the triisopropyl-phenyl derivative (**1**) with $[Rh(nbd)Cl]_2$ resulted in the formation of Rh(nbd)(**1**)Cl (**1c**) (δ, 32.7 ppm, $^{1}J(Rh–P) = 138$ Hz). After 4 days a pair of doublets (vide supra) (δ, 57.3 ppm, 80.3 ppm, 37.8 Hz) appeared (even under very inert conditions) which was assigned to the analogous dimer dioxide, **1**′ (Fig. 3).

The most basic **4** shows different coordination chemistry towards $[Rh(nbd)Cl]_2$. Neither unreacted phosphole ligand nor cyclodimerization products could be observed when **4**/Rh = 2/1 ratio was used. A complex showing a doublet (δ, 26.6 ppm, $^{1}J(Rh–P) = 114$ Hz) was the only detectable species a few minutes after starting the reaction. It was assigned to the $[Rh(nbd)(\mathbf{4})_2]^+$ cation. This result is in agreement with the earlier findings obtained with monophosphines.

Table 4
Hydroformylation of styrene in the presence of platinum and rhodium catalysts[a]

Catalyst	R. time (h)	Conversion (%)	R_C[b] (%)	R_{br}[c] (%)
$PtCl_2(PhCN)_2$ + **1** + $SnCl_2$	130	21	81	28.5
$PtCl_2(PhCN)_2$ + **2** + $SnCl_2$	130	11	81	63
$PtCl_2(PhCN)_2$ + **4** + $SnCl_2$	130	48	90	85.5
$PtCl_2(PhCN)_2$ + **9** + $SnCl_2$	130	3	87	70
$[Rh(nbd)Cl]_2$ + **1**	20	99	99	80.5
$[Rh(nbd)Cl]_2$ + **4**	10	61	98.5	58

[a] Reaction conditions: 0.05 mmol catalyst, Pt/P/$SnCl_2$ = 1/2/1; Rh/P = 1/2; 100 mmol styrene; solvent: toluene; $p(CO) = p(H_2) = 40$ bar; reaction temperature: 100°C.
[b] Chemoselectivity; (mol **6** + mol **7**)/(mol **6** + mol **7** + mol **8**) × 100.
[c] Regioselectivity; (mol **6**)/(mol **6** + mol **7**) × 100.

2.4. Homogeneous hydroformylation of styrene with platinum- and rhodium-containing catalysts

Styrene (**5**) as a model substrate was allowed to react in the presence of 'in situ' platinum- and rhodium-containing catalysts prepared from $PtCl_2(PhCN)_2$ and the corresponding ligand (Table 4).

$$PhCH{=}CH_2\ (\mathbf{5}) \xrightarrow{CO/H_2} PhCH(CH_3)CHO\ (\mathbf{6}) + Ph(CH_2)_2CHO\ (\mathbf{7}) + PhC_2H_5\ (\mathbf{8})$$

In addition to the formyl regioisomers **6** and **7,** the hydrogenation product **8** was also formed in all cases.

Although the catalytic activity of the above platinum catalysts containing monophospholes and especially that of the in situ system containing the cyclodimer diphosphine (**9** [21], Fig. 4) is very low, their tests are of theoretical importance, since the use of sterically hindered monophospholes and 7-phospha-norbornene type ligands in homogeneous catalysis is unprecedented.

It is worth noting that both the chemo- and regioselectivities of hydroformylation are influenced by the basicity of the phosphole ligands. The use of the more basic ligand (**1**) in platinum-containing catalyst results in low chemo- and regioselectivities, 81 and 28.5%, respectively (regioselectivity towards branched aldehyde regioisomer was defined). While the chemoselectivity is nearly the same in the case of **2**, the regioselectivity is substantially improved, i.e. the formation of the

branched aldehyde is favoured. A further increase in both selectivities was achieved by the application of **4** resulting in 90% and 85.5% chemo- and regioselectivity, respectively.

The use of the diphosphine **9** (Fig. 4) resulted in negligible activity (less than 3% conversion in 130 hours) in platinum-catalysed hydroformylation.

However, the highly active rhodium-containing in situ systems containing both **1** and **4** provide the expected high chemoselectivity. The 'branched selectivity' decreased dramatically when **4** was substituted for **1**.

3. Experimental

3.1. Chemicals

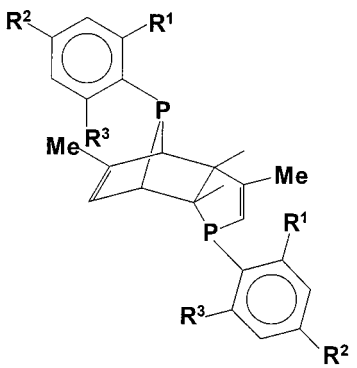
The 1-arylphosphole ligands (**1**, **2** and **3**) were synthesised as described earlier [17–19]. The synthesis of **9** has been published recently [21]. Platinum (II)chloride was purchased from Aldrich. Benzene was distilled under argon from sodium in the presence of benzophenone.

The $PtCl_2(PhCN)_2$ precursor was prepared as described previously [22]. The $PtCl_2(L_2)$ complexes were prepared in refluxing benzene by the widely used 'benzonitrile method' [22].

3.2. Instrumentation

^1H- 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.



9 $R^1=R^2=R^3=Me$

Fig. 4. Diphosphine **9**.

3.3. Preparation of trans-$PtCl_2$(**1**)$_2$

In a typical experiment 0.1 mmol of $PtCl_2(PhCN)_2$ was dissolved in 8 ml refluxing benzene, and a solution of 0.1 mmol **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 isolated by filtration, after the mixture was cooled to room temperature. The product was recrystallysed from benzene. Analysis for $PtCl_2$(**1**)$_2$: Anal. Calc: C, 55.42; H, 6.74; Cl, 8.18; Found: C, 55.77; H, 6.91; Cl, 7.93.

3.4. Hydroformylation experiments

In a typical experiment a solution of 0.025 mmol of $PtCl_2(PhCN)_2$, 0.05 mmol of monophosphole and 0.05 mmol of $SnCl_2$ in 30 ml toluene containing 0.1 mole of styrene was transferred under argon into a 150 ml stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath and the mixture was stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC.

Acknowledgements

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