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Carbonylation (hydroformylation and hydroalkoxycarbonylation) of styrene in the presence of transition metal–ferrocene-based aminophosphine systems

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Abstract

The $PtCl_2$(L)-type platinum complexes of the ferrocenyl ligands, (S_c,S_m)-1-diphenylphosphino-α-*N*,*N*-dimethylamino[2,3]tetramethyleneferrocene (**1**) and (S_c,S_m)-1,1′-bis(diphenylphosphino)-α-*N*,*N*-dimethylamino[2,3]tetramethylene ferrocene (**2**) have been synthesised. Both the 'preformed' and in situ catalysts have been used in hydroformylation of styrene. In spite of low enantioselectivities and activities, the ferrocenyl based systems proved to be of interest from theoretical point of view. The ligand influence on regio- and enantioselectivity has been investigated in systems containing either only one of the ferrocenyl ligands or one ferrocenyl ligand together with bdpp ((2*S*,3*S*)-2,4-bis(diphenylphosphino)pentane). The coordination of the respective ligands to platinum in the catalytic process can be deduced from results obtained with the 'mixed ligand system'. The rhodium in situ catalysts containing either **1** or **2** are active in hydroformylation but the ee-s obtained with styrene are low. In the presence of ligand **1**, the palladium-catalysed hydromethoxycarbonylation of styrene resulted in the predominant formation of the branched regioisomer, in case of **2** mostly the linear product was formed.

Keywords: Carbonylation; Hydroformylation; Platinum; Palladium; Ferrocene; Phosphine; Nuclear magnetic resonance

1. Introduction

The importance of carbonylation reactions has been documented in numerous studies, reporting mainly on applications in organic synthesis or on reaction mechanisms [1]. Among these reactions hydroformylations (and hydroalkoxycarbonylations) predominate [2]. In particular, a large number of simple and functionalised olefins have been investigated with respect to products of practical interest [3]. Large efforts have been made in order to apply asymmetric hydroformylation reactions to the synthesis of chiral building blocks and of biologically important derivatives [4].

A number of mono- and bidentate phosphines have been used as both chiral and achiral ligands in transition metal complexes showing hydroformylation and/or hydroalkoxycarbonylation activity [5]. Especially chiral diphosphines of C_2 symmetry have been investigated thoroughly as ligands in asymmetric hydroformylation reactions [6–12]. Diphosphines possessing diphenylphosphino groups in different environments have also been reported as efficient ligands [13]. However, recent studies with heterobidentate ligands show the importance of different donor atoms in rhodiumcatalysed reaction [14,15].

Ferrocene-based chiral phosphines and aminophosphines form transition metal complexes which have already been identified as active catalysts in a variety of enantioselective reactions including hydrogenation, hy-

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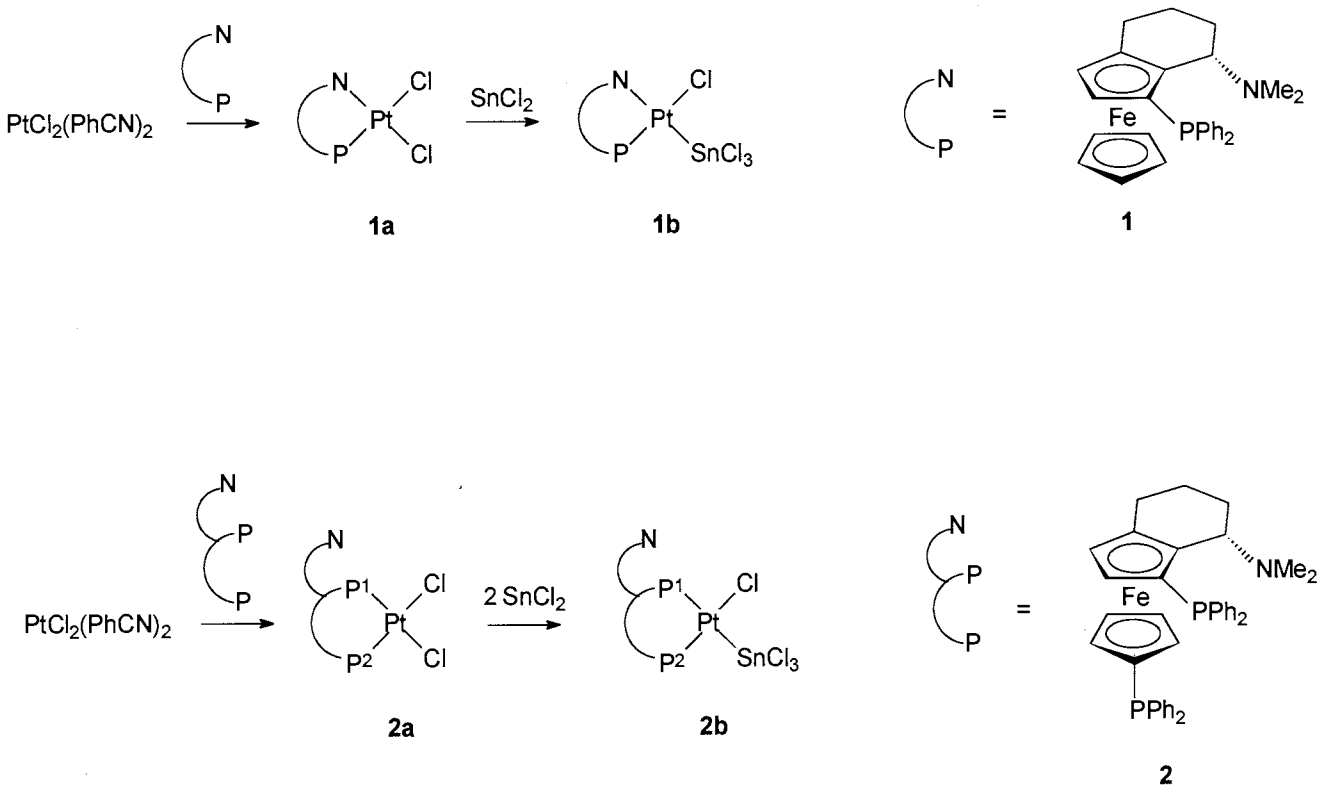

Fig. 1. The synthesis of platinum complexes containing ferrocenyl ligands, **1** and **2**.

drosilylation, cross-coupling reactions and aldol condensation [16,17]. Surprisingly, to the best of our knowledge, no example for their applicability in enantioselective carbonylation reactions has been reported, yet.

In this paper we describe the synthesis and characterisation of palladium and platinum complexes modified with enantiopure homoannularly bridged ferrocenyl aminophosphine or aminobisphosphine ligands and discuss their application in hydroformylation and hydroalkoxycarbonylation reactions.

2. Results and discussion

2.1. Synthesis and characterisation of palladium and platinum complexes

The ferrocenyl ligands ((*S*$_c$,*S*$_m$)-1-diphenylphosphino-α-*N*,*N*-dimethylamino[2,3]-tetramethyleneferrocene (**1**) and (*S*$_c$,*S*$_m$)-1-1′-bis(diphenylphosphino)-α-*N*,*N*-dimethylamino[2,3]tetramethyleneferrocene (**2**) [18–20]) were reacted with $PtCl_2(PhCN)_2$ precursor resulting in easily accessible **la** and **2a**, respectively (Fig. 1). Ligand **1** forms a P–N chelating platinum complex by replacing benzonitrile ligands of the respective precursors. However, on reacting with $PtCl_2(PhCN)_2$ the P–P–N derivative (**2**) acts as diphosphine leaving the amino functionality uncoordinated. In case of palladium, with ligand **1** also the P–N complex (**1c**) is formed but with **2** depending on the reaction conditions, a P–P complex or a $Pd_3(\mathbf{2})_2$-type complex (**2c**) is isolated. In the latter case each ferrocene entity (**2**) forms a P–N chelate with one $PdCl_2$ unit while the third palladium bridges the ferrocenes via the *trans* coordinating PPh_2 functionalities bound to the monosubstituted Cp-rings. The synthesis and characterisation of the Pd complexes of both ligands have been reported earlier [18,20,21].

Both the chemical shifts and coupling constants listed in Table 1 reflect the different types of coordination in complexes **1a** and **2a**. In case of **1a** the coordination of nitrogen was proved by the Pt satellites of the proton signals ($^3J(^{195}Pt,^1H) = 26$ Hz, $^3J(^{195}Pt,^1H) = 30$ Hz) of the NMe_2 methyl groups. In addition, the large difference in the chemical shifts $\delta(^{31}P)$ of **1a** and **2a** is indicative of a P–N coordination in **1a**.

The configuration of complex **1b** could also be deduced from the NMR data. From the coupling constants $J(^{31}P,^{117}Sn)$ and $J(^{31}P,^{119}Sn)$ (186 and 195 Hz, respectively) it follows that in case of **1a** tin(II)chloride is inserted into the Pt–Cl bond *trans* to nitrogen giving **1b** with the trichlorostannato ligand *cis* to phosphorus.

The 'high-field' phosphorus signal of **2a** was assigned to the phosphorus bound to the Cp-ring possessing the homoannularly bridged dimethylamino group. The insertion of $SnCl_2$ most likely takes place into Pt–Cl bond *trans* to this phosphorus (P^1) which is indicated by the downfield shift of 2.2 ppm of this signal due to

Table 1
^{31}P-NMR data of Pt complexes containing ferrocenyl ligands, **1** and **2**

Complexes		δP	$^{1}J(^{195}Pt,^{31}P)$	$J(P^1,P^2)$	$^{2}J(^{31}P,^{117}Sn)$	$^{2}J(^{31}P,^{119}Sn)$
		ppm	Hz	Hz	Hz	Hz
$PtCl_2$(1)	(**1a**)	−10.0	4025	—	—	—
$PtCl(SnCl_3)$(**1**)	(**1b**)	2.0	2933	—	186	195
$PtCl_2$(**2**)	(**2a**)	$\delta P^1 = 14.5$	4034	7.2	—	—
		$\delta P^2 = 19.2$	4012			
$PtCl(SnCl_3)$(**2**)	(**2b**)	$\delta P^1 = 16.7$	3843	4.8	n.a.	n.a.
		$\delta P^2 = 18.9$	3881			

the strong *trans*-influence of the trichlorostannato ligand. (The chemical shift of the other phosphorus (P^2) practically remained unchanged.) Because of the low resolution due to the low solubility of **2b** neither the *cis* nor the *trans* coupling of ^{117}Sn and ^{119}Sn can be observed. It is worth noting that in the synthesis of **2b** two-fold excess of tin(II)chloride was needed to accomplish the insertion reaction. This fact is probably due to the coordination of tin(II)chloride to the noncoordinated *N*-arm.

2.2. Hydroformylation of styrene with platinum- and rhodium-containing catalysts

Styrene (**3**) as model substrate was reacted in the presence of in situ catalysts (prepared either from rhodium containing precursor ($[Rh(nbd)Cl]_2$) and ligands **1** or **2**, or platinum containing precursor ($PtCl_2$(**1**) or $PtCl_2$(**2**)) and anhydrous tin(II)chloride) with CO/H_2 (1/1) at 60–100°C, under a pressure of 80 bar (Table 2).

$$PhCH{=}CH_2 \xrightarrow[60-100^{o}C]{CO/H_2} PhCH(CH_3)CHO + Ph(CH_2)_2CHO + PhC_2H_5 \quad (1)$$

The catalytic activities of the rhodium-**1** and rhodium-**2** in situ systems are much higher than those observed for **1a**-$SnCl_2$ and **2a**-$SnCl_2$ catalysts. The rhodium- and platinum-containing catalytic systems yielded strikingly different product distributions. Both chemo- and regioselectivity towards branched aldehyde (**4**) are much higher when rhodium-containing systems are used. The formation of hydrogenated product (**6**) is almost negligible in this case. The ee-s obtained with both rhodium and platinum catalysts are extremely low.

However, enantioselectivity could be slightly increased by the addition of bdpp ((2*S*,3*S*)-2,4-bis(-diphenylphosphino)pentane). The higher activity observed in this case shows the interplay of ferrocene-type ligands and bdpp. The absolute configuration of the predominating enantiomer of **4** was found to be R when the **1b**-(2*S*,4*S*)bdpp-$SnCl_2$ system was applied. The ee-s are undoubtedly higher than those obtained with Pt-(2*S*,4*S*)-bdpp-$SnCl_2$ system [10]. In case of **1a**-(2*S*,4*S*)-bdpp-$SnCl_2$ neither the absolute configuration nor the ee are characteristic for the bdpp containing system. It can be stated that the results obtained with catalytic systems containing 'mixed ligands' (**1** and bdpp or **2** and bdpp) are substantially different from those obtained with **1a** or **2a**. Since the catalytic results are characteristic neither for the bdpp- nor the ferrocenyl-containing systems, and furthermore, the activities are between the two systems **1a** and $PtCl_2$(bdpp), during the catalytic reaction a coordination of both ligands to platinum can be assumed in the 'mixed ligand' system. (In chiral diphosphine–monophosphine systems the unexpected effect of the ligands on ee-s have already been observed in hydrocarbalkoxylation [22], hydrogenation [23] and hydroformylation [24].) The reason for the observed results could be a monodentate coordination of the potentially bidentate ligands **1** and **2** in the transition state complex responsible for the stereochemical outcome of the reaction.

Both the low activity and enantioselectivity obtained in the presence of **1** and **2** indicate that the bite angles of the ferrocenyl ligands are too small upon coordination to rhodium(I) and platinum(II) possessing relatively large ionic radius. Furthermore, the amine functionality of the ligands might be responsible for $HSnCl_3$ abstraction from the $PtH(SnCl_3)(L)$ catalytic intermediates by reductive elimination and resulted in the formation of an ammonium salt, $RNMe_2 \cdot HSnCl_3$ [25]. Therefore, the expected favourable effect of the hemilabile P–N ligands might be strongly diminished by blocking one of the chelate donor atoms.

Catalyst precursors prepared in situ from complex $PdCl_2$(**1**) and ligand **1** or complex $(PdCl_2)_3$(**2**)$_2$ and ligand **2** have been tested in hydromethoxycarbonylation of styrene (Eq. 2).

$$PhCH(CH_2 \xrightarrow{CO/CH_3OH} PhCH(CH_3)COOCH_3 + Ph(CH_2)_2COOCH_3 \quad (2)$$

In all cases both regioisomers were formed but the regioselectivities are completely different depending on the two catalytic precursors used (Table 2). While in the

Table 2
Hydroformylation and hydromethoxycarbonylation of styrene using ferrocenyl ligands, **1** and **2**[a]

Catalyst	R. time	T	Conv.	R_c^b	R_{br}^c	e.e.
	[h]	[°C]	[%]	[%]	[%]	[%]
$PtCl_2$(**1**)+$SnCl_2$	100	80	89	74	58	n.a.
$PtCl_2$(**1**)+bdpp+$SnCl_2$	30	80	79	93	32	21 (S)
$PtCl_2$(**1**)+bdpp+$SnCl_2$	15	100	90	83	60	7 (S)
$PtCl_2$(**2**)+$SnCl_2$	80	80	49	88	51	3 (S)
$PtCl_2$(**2**)+bdpp+$SnCl_2$	15	90	98	88	33	7 (R)
[Rh(nbd)Cl]$_2$+**1**	14	60	38	99	94	0.5 (R)
[Rh(nbd)Cl]$_2$+**2**	14	60	76	99	89	2 (S)
$PdCl_2$(**1**)+**1**	180	110	100	71	—	
$(PdCl_2)_3$(**2**)$_2$+**2**	450	110	50	100	28	—

[a] Reaction conditions: 0.025 mmol $PtCl_2$(1igand); 0.05 mmol $SnCl_2$; 30 ml toluene; 100 mmol styrene; p(CO) = p(H_2) = 40 bar (in hydroformylation) 0.04 mmol $PdCl_2$(1igand); 0.02 mmol ligand; 16 mmol styrene, 10 ml toluene; 5 ml methanol; 130 bar CO (in hydromethoxycarbonylation).
[b] (**4**+**5**)/(**4**+**5**+**6**)×100 (for hydroformylation).
[c] **4**/(**4**+**5**)×100 (for hydroformylation); **7**/(**7**+**8**)×100 (for hydromethoxycarbonylation).

presence of **1** the branched regioisomer (**7**) predominates, the application of ligand **2** resulted in the formation of the linear ester (**8**) as the main product. The results are similar to those obtained with monodentate and bidentate phosphines, respectively. Although in the trinuclear catalytic precursor, **2c** ($(PdCl_2)_3$(**2**)$_2$ [20,21]) two of the palladium atoms contain P–N coordinated ligands and the third one shows *trans*-monodentate type coordination, upon addition of the free ligand (**2**), the PP bidentate coordination can not be excluded under catalytic conditions.

As a conclusion it can be stated, that the rather rigid ferrocenyl ligands possessing a relatively small bite angle (especially when bound to platinum) are not sufficiently active in carbonylation reactions. A systematic investigation of the influence of ferrocenyl ligand structure on carbonylation activity is in progress.

3. Experimental

The catalytic precursors $PtCl_2(PhCN)_2$, $PdCl_2(PhCN)_2$ and [Rh(nbd)Cl]$_2$ were prepared as described previously [26,27]. Toluene was distilled under argon from sodium in the presence of benzophenone. Styrene was freshly distilled before use. Anhydrous tin(II)chloride was prepared by dehydrating $SnCl_2 \cdot 2H_2O$ with a stoichiometric amount of acetic anhydride, followed by washing with dry diethyl ether.

The ^{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. The chemical shifts were reported relative to tetramethylsilane and H_3PO_4, respectively. The samples were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1. The elemental analyses were performed on a 1108 Carlo Erba apparatus.

3.1. Synthesis of $PtCl_2$(**1**) (**1a**) and $PtCl_2$(**2**) (**2a**)

A 0.2 mmol amount of $PtCl_2(PhCN)_2$ was dissolved in 16 ml refluxing benzene, and a solution of 0.2 mmol **1** (or **2**) in 4 ml of benzene was added. The experiment was conducted for 2 h. A dark yellow solid was formed, which was filtered off after the mixture was cooled to r.t.. The product was washed with cold benzene. The yields were 90 and 80% for **1a** and **2a**, respectively.

1a: ^{1}H-NMR ($CDCl_3$, 300 MHz, TMS): (selected data) 3.45 (s with broad Pt satellites, J(Pt,CH_3) = 26 Hz; 3H, NCH_3); 3.68 (s with broad Pt satellites, J(Pt,CH_3) = 30 Hz, 3H, NCH_3); 3.85 (t, J = 4 Hz, 1H, Cp-H); 4.22 (s, 5H, Cp); 4.58 (d, J = 4 Hz, 1H, Cp-H); ^{31}P-NMR ($CDCl_3$, 121.4 MHz, H_3PO_4): see Table 1. Analysis calculated for $C_{28}H_{30}NPCl_2FePt$ (M = 733.36): C, 45.86; H, 4.12; N, 1.91; Found: C, 45.98; H, 4.31; N, 2.05%; yield: 90%.

2a: ^{1}H-NMR ($CDCl_3$, 300 MHz, TMS): (selected data) 1.90 (s, 6H, N(CH_3)$_2$); 3.82 (m, 1H, Cp-H); 4.20 (m, 1H, Cp); 4.35 (m, 2H, Cp-H); 4.55 (m, 1H, Cp-H); 4.60 (m, 1H, Cp-H); ^{31}P-NMR ($CDCl_3$, 121.4 MHz, H_3PO_4): see Table 1. Analysis calculated for $C_{40}H_{39}NP_2Cl_2FePt$ (M = 917.54): C, 52.36; H, 4.28; N, 1.53; Found: C, 52.44; H, 4.42; N, 1.70; yield: 80%.

3.2. Hydroformylation experiments

In a typical experiment a solution of 0.025 mmol of $PtCl_2$(**1**) and 0.05 mmol of $SnCl_2$ in 30 ml toluene containing 0.1 mol of styrene was transferred under argon into a 150 ml stainless steel autoclave. The reaction vessel was pressurised to 80 bar total pressure (CO/H_2 = 1/1) and placed in an oil bath and the mixture 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. After a fractional distillation the specific rotation of the 2-phenylpropanal fraction was measured.

3.3. Hydromethoxycarbonylation experiments

In a typical experiment 0.04 mmol of $PdCl_2$(**1**) and 0.02 mmol of **1** was measured into a 150 ml stainless steel autoclave and charged with 1.8 ml styrene, 10 ml toluene and 5 ml methanol under argon atmosphere. The reaction vessel was pressurised to 130 bar CO pressure and placed in an oil bath and the mixture stirred magnetically. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the dark red solution was removed and immediately analysed by GC.

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