Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 353 (2003) 301–305

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Note

NMR investigation of platinum–diphosphine complexes in [BMIM][PF_6] ionic liquid

Gábor Rangits [a], György Petőcz [a], Zoltán Berente [b,c], László Kollár [a,c,*]

[a] Department of Inorganic Chemistry, University of Pécs, Ifjúság u. 6, P.O. Box 266, H-7624 Pecs, Hungary
[b] Institute of Biochemistry, University of Pécs, P.O. Box 99, H-7643 Pecs, Hungary
[c] Research Group for Chemical Sensors of the Hungarian Academy of Sciences, P.O. Box 266, H-7624 Pecs, Hungary

Received 29 November 2002; accepted 10 March 2003

Abstract

The formation of platinum–diphosphine complexes of catalytic importance was investigated in [BMIM][PF_6] (BMIM = butyl-methyl-imidazolium cation) ionic liquid by NMR for the first time. Both the PtCl($SnCl_3$)(bdpp) and Pt$(SnCl_3)_2$(bdpp) complexes (where bdpp = 2,4-bis(diphenylphosphino)pentane) were identified in the insertion reaction of tin(II)chloride into the Pt–Cl bond of $PtCl_2$(bdpp) complex. The addition of PPh_3 to $PtCl_2$(bdpp) resulted in the formation of $[Pt(bdpp)(PPh_3)Cl]^+$ complex cation as a minor component, which turned to be a major component in the presence of tin(II)chloride while it forms trichlorostannate counterion. Both types of reactions show *high similarity with those obtained in conventional organic solvents*. As a serious disadvantage of the use of [BMIM][PF_6] as ionic liquid, the partial decomposition of the hexafluorophosphate counterion in the presence of the smallest amount of water (and tin(II)chloride) is also discussed.

Keywords: Platinum; Phosphine; Ionic liquid; Nuclear magnetic resonance; Ligand exchange

1. Introduction

Fused salts are liquids containing only ions and are often called ionic liquids. Especially those ones, that are liquid at room temperature, provide a useful extension to the range of solvents that are used by synthetic chemists. Although these ionic liquids possess a number of physical properties that make them interesting for a wide audience of chemists, it is only in the past few years that significant literature has become available [1]. Excellent reviews and papers appeared quite recently showing the potential of ionic liquids both in classical organic reactions like Friedel–Crafts alkylation and homogeneous catalysis [2–4].

The application of ionic liquids in transition metal catalysed reactions turned up in the middle of the nineties, and reviewed recently [5]. The chloroaluminate and ethylchloroaluminate ionic liquids have been successfully used as solvents for the nickel catalysed dimerization of propene [6], for the dimerization of butenes [7] and ethene [8] and for the rhodium catalysed hydrogenation of cyclohexene [9].

Due to the high practical importance of hydroformylation, the 'ionic liquid version' has been investigated as early as 1972 by Parshall who described the platinum-catalysed hydroformylation of ethene in [NEt_4][$SnCl_3$] melts [10].

Room temperature ionic liquid, [BMIM][PF_6] (BMIM = butyl-methyl-imidazolium cation) (Fig. 1), whose application could bring a real breakthrough in this field, proved to be a good solvent in rhodium-catalysed hydroformylation of 1-pentene (catalyst: [$Rh(CO)_2$(acac)]/PPh_3) [11] and long-chain α-olefins [12]. In the latter case a cationic cobaltocenium ligand has been used. Wasserscheid and Waffenschmidt did a seminal work in the field of platinum-catalysed hydroformylation in [BMIM][$SnCl_3$] [13].

Although several types of catalytic reactions have been studied, sporadic results were published concerning even the simplest reactions of complexes in ionic liquid.

---

* Corresponding author. Tel.: +36-72-32 7622/4153; fax: +36-72-50 1527.
E-mail address: kollar@ttk.pte.hu (L. Kollár).

0020-1693/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0020-1693(03)00291-3

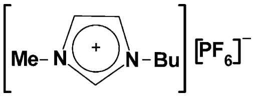


Fig. 1. The structure of the [BMIM][PF_6] ionic liquid.

Therefore, our results on kinetically relatively inert platinum–phosphine–tin(II)chloride systems, also of potential catalytic importance, will be presented. Furthermore, the preliminary results on potential side reactions of the [BMIM][PF_6] ionic liquid will also be discussed.

2. Results and discussion

2.1. NMR investigations on platinum–diphosphine–tin(II)chloride complexes in ionic liquids

The solution structure of well-known hydroformylation catalysts, platinum(II)-bdpp-tin(II)chloride in situ catalytic systems, as well as that of the PtCl($SnCl_3$)(bdpp) precursors were investigated in [BMIM][PF_6] ionic liquid. The NMR data are summarised in Table 1.

One of the key-points of the platinum catalysed hydroformylation is the role of tin(II)chloride. It has been proved by detailed high pressure NMR investigation that it acts as a counterion in the elementary steps of the hydroformylation reaction [14]. Its insertion into the Pt–Cl bond of various *cis*- and *trans*-Pt(tertiary phosphine)$_2Cl_2$ complexes was investigated in detail as early as 1978 by Pregosin and Sze [15]. The extent of the formation of the corresponding PtCl($SnCl_3$)(diphosphine) complexes is highly solvent dependent. In chloroform or dichloromethane the tin(II)chloride insertion takes place nearly quantitatively resulting in the formation of the corresponding trichlorostannato complexes.

However, in [BMIM][PF_6] ionic liquid the $PtCl_2$(bdpp) complex (**1**) shows a limited reactivity towards $SnCl_2$ (anhydrous) even at higher temperature (70 °C) and elevated reaction time (50 h). Up to 15% of the starting complexes have been converted to the corresponding trichlorostannato complex (**1a**). However, when PtCl($SnCl_3$)(bdpp) (bdpp = 2,4-bis(diphenylphosphino)pentane) **1a** was prepared in crystalline form and a twofold excess of $SnCl_2$ was added, a mixture of $PtCl_2$(bdpp) **1**, Pt($SnCl_3$)$_2$(bdpp) **1b**, and the starting complex, **1a** has been obtained (Scheme 1). Following the reaction by ^{31}P NMR, the composition of the mixture was found temperature dependent. By increasing the temperature, the amount of **1b** was slightly increased (Fig. 2), so the equilibrium was shifted towards the formation of trichlorostannato species, **1a** and **1b**. Although the determination of the extremely weak $^{117,119}Sn$ satellites could have been done with high uncertainty, the prior information on Pt–$SnCl_3$ complexes (e.g. the relative downfield shifts and the magnitude of ^1J(Pt,P) coupling constants assigned to phosphorus *trans* to chloro or trichlorostannato ligand) enables the identification of these species. However, even by using the threefold excess of tin(II)chloride, unlike the reaction in $CDCl_3$, neither the formation of **1a** nor that of **1b** are complete.

It has to be noted, that tin(II)chloride insertion takes place to much smaller extent with $PtCl_2$(*chiraphos*) **2** and $PtCl_2$(*prophos*) **3** (where *chiraphos* and *prophos* stands for 2,3-bis(diphenylphosphino)butane and 1,2-bis(diphenylphosphino)propane, respectively). Similar situation has been observed with $PtCl_2$(*cis*-1,2-bis(di-

Table 1
NMR data of Pt-diphosphine complexes in [BMIM][PF_6] ionic liquid

Complexes		$\delta(^{31}P)$ (ppm)	$^1J(^{31}P,^{195}Pt)$ (Hz)	$^2J(^{31}P,^{31}P)$ (Hz)	$\delta(^{13}C)$ [a] (ppm)	$^1J(^{13}C,^{195}Pt)$ (Hz)	$^2J(^{13}C,^{13}C)$ (Hz)
$PtCl_2$(bdpp)	**1**	8.5	3431	–			
PtCl($SnCl_3$)(bdpp)	**1a**	9.1	3370	24.4			
		5.0	3121	24.4			
Pt($SnCl_3$)$_2$(bdpp)	**1b**	10.6	3350 ± 8 [b]	–			
$[Pt(bdpp)(PPh_3)Cl]^+$	**1c**	27.2	2403 ± 8 [b]	390; 15.0			
		18.4	2300 ± 8 [b]	390; 28.0			
		15.8	3500 ± 8 [b]	15.0; 28.0			
$[Pt(bdpp)(PPh_3)Cl]^+$ [c]	**1c**	22.1	2368	392; 20.0			
		14.6	2309	392; 25.4			
		12.1	3454	20.0; 25.4			
$[Pt(bdpp)_2]^{2+}$	**1d**	9.0	2233				
Pt(^{13}CN)$_2$(bdpp)	**1e**	3.4	2380	28.2	126.4	1022	25.0
		2.6	2384		127.7	1025	

Solvent: [BMIM][PF_6]; ^{31}P NMR and ^{13}C NMR spectra were recorded at 161.9 and 100.6 MHz, respectively (temperature: 70 °C).

[a] Chemical shift of the CN carbon.

[b] Due to the Pt-satellites of very low intensity, the ^1J(Pt,P) coupling constants could be determined with a given deviation, only.

[c] ^{31}P NMR in $CDCl_3$ (see Ref. [16]).

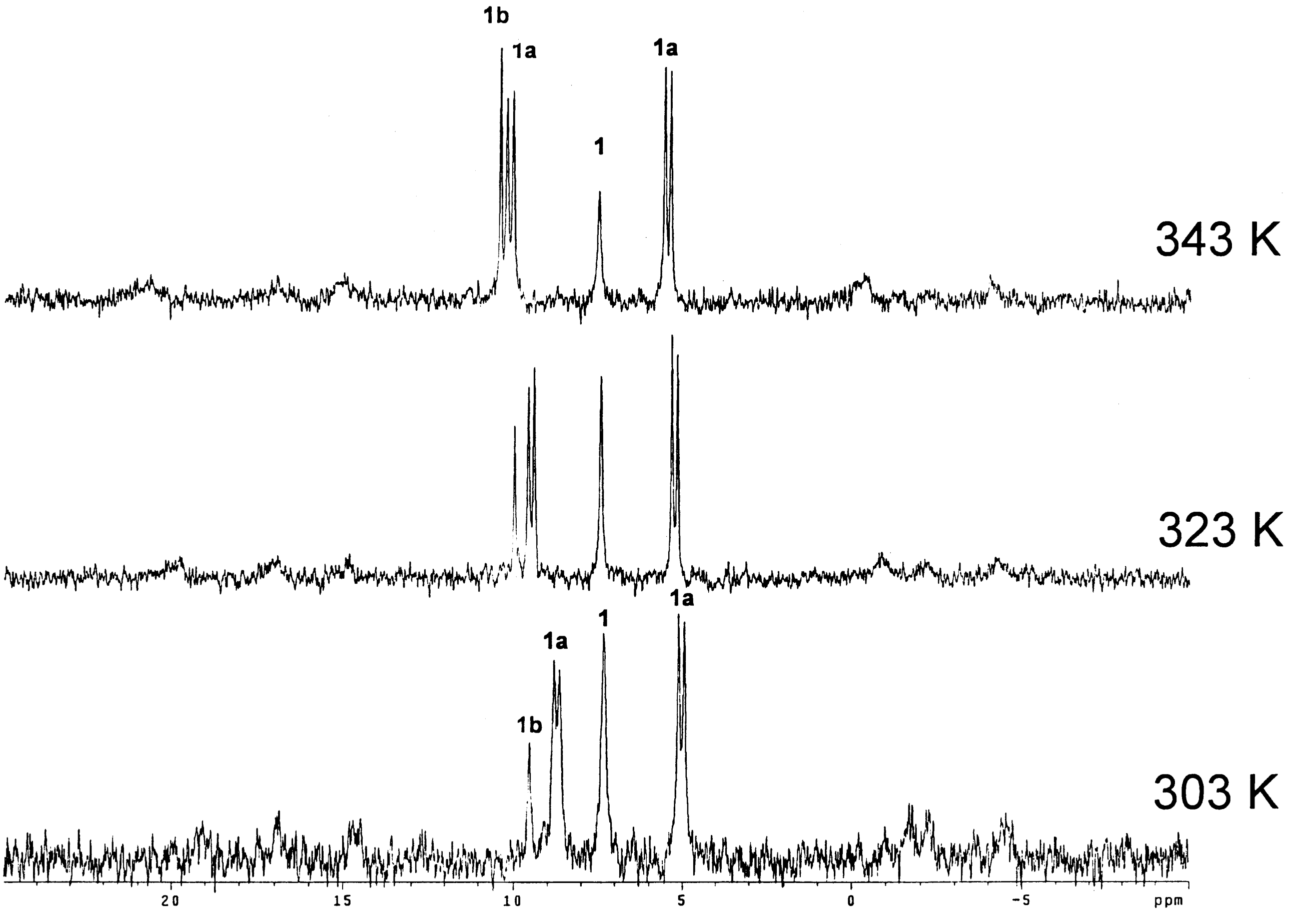


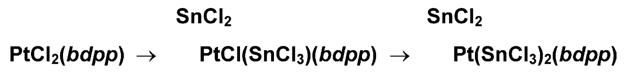
Fig. 2. The ^{31}P NMR of the complexes formed in the reaction of $PtCl_2(bdpp)$ and $SnCl_2$ in $[BMIM][PF_6]$ at 303, 323 and 343 K (see also Scheme 1).

phenylphosphino)ethene), where the five-membered platinum–phosphine chelate-ring is even more rigid than in **2** and **3**.

2.2. *NMR investigations of ligand exchange reactions with platinum–diphosphine complexes in [BMIM][PF$_6$] ionic liquid*

In order to investigate some ligand-exchange reactions in ionic liquid, 1 equiv. of PPh_3 was added to **1a**. Although some 'P_2-complexes' **1**, **1a**, **1b**, featuring the approximately 20–28% of the total amount of complexes, remained in the reaction mixture, $[Pt(bdpp)(PPh_3)Cl][SnCl_3]$ (**1c**) containing both bidentate and monodentate phosphines coordinated in a square-planar arrangement, has been formed as a major product (Scheme 2). Both the chemical shifts and coupling constants correspond to those obtained in chloroform [16]. It has to be noticed that platinum satellites are *inherently broader* than the 'central line', and are extremely broad and weak in ionic liquid. In certain cases their assignment cannot be done with usual accuracy (e.g. for $CDCl_3$ solutions) due to the low resolution (*high viscosity* even at 70 °C) and *low solubility* of the complex in ionic liquid (Fig. 3, Table 1). However, perfect resolution of the signals due to both the $^{2}J_{cis}(P,P)$ and $^{2}J_{trans}(P,P)$ coupling constants of diagnostic value can be achieved at 70 °C.

Upon addition of 1 M equiv. of bdpp and 2 M equiv. of $SnCl_2$ to **1**, the quantitative formation of $[Pt(bdpp)_2](SnCl_3)_2$ was observed (Scheme 3, Table 1). It has to be mentioned, that the reaction resulting in the same complex cation **1d** is complete upon addition of **1** equiv. of $SnCl_2$ only. This result shows clearly, that in case of a favourable six-membered chelate ring even the formation of a good leaving ligand, $SnCl_3^-$ is not a precondition of the formation of 'PtP_4' cationic species. The chloro ligand could also fully dissociate and form a chloride counterion.



$$\underset{\mathbf{1}}{PtCl_2(bdpp)} \xrightarrow{SnCl_2} \underset{\mathbf{1a}}{PtCl(SnCl_3)(bdpp)} \xrightarrow{SnCl_2} \underset{\mathbf{1b}}{Pt(SnCl_3)_2(bdpp)}$$

Scheme 1. Insertion of $SnCl_2$ into Pt–Cl bond.

$$\underset{\mathbf{1}}{PtCl_2(bdpp)} + PPh_3 + SnCl_2 \rightarrow \underset{\mathbf{1c}}{[Pt(bdpp)(PPh_3)Cl][SnCl_3]}$$

Scheme 2. Formation of Pt-bdpp-monophosphine cation.

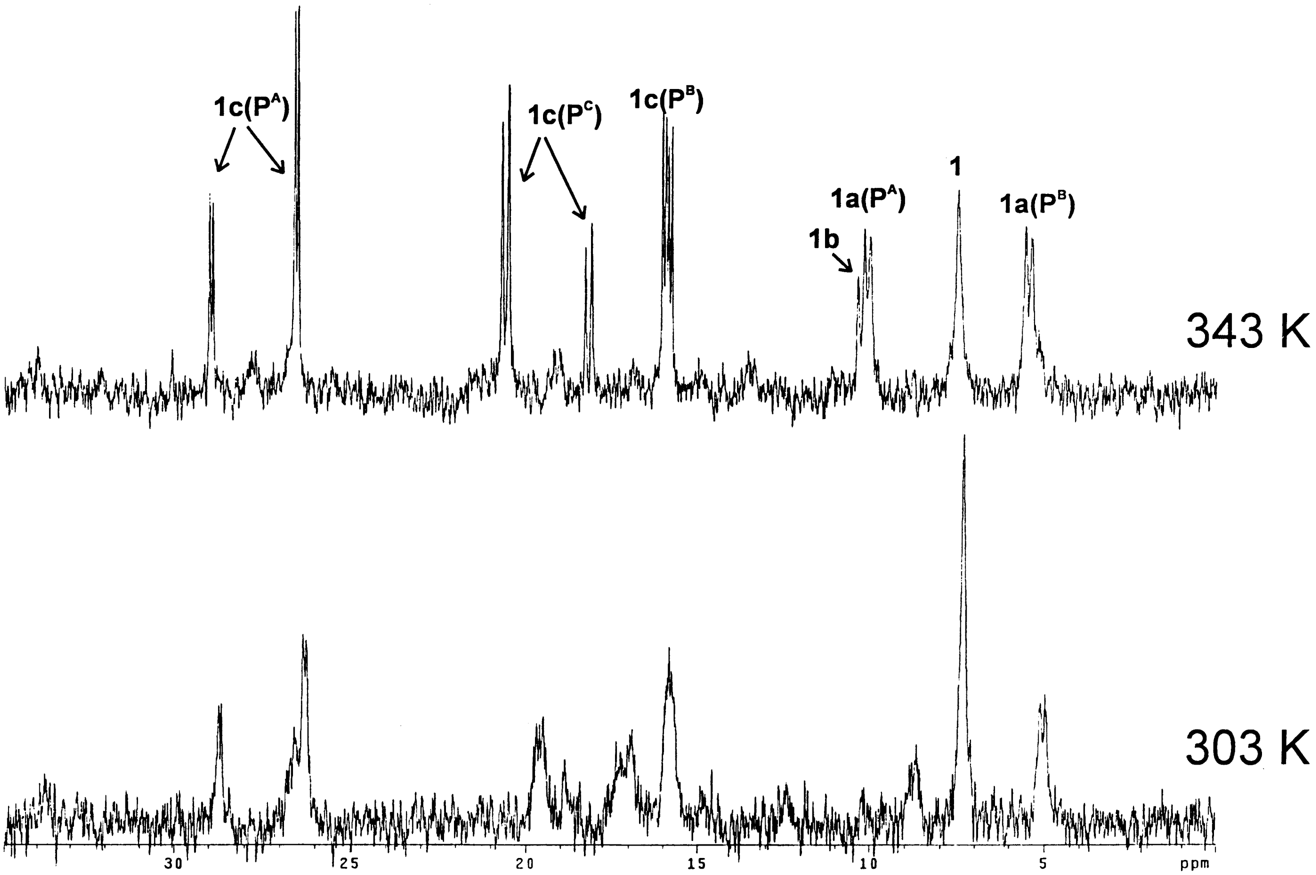


Fig. 3. The ^{31}P NMR of the complexes formed in the reaction of $PtCl_2$(bdpp), $SnCl_2$ and PPh_3 in [BMIM][PF_6] at 303 and 343 K (see also Scheme 2).

Similarly, complete ligand exchange reaction has been observed with 2 M equiv. of $Na^{13}CN$. The resulting [Pt(bdpp)(^{13}CN)$_2$] complex (**1e**) shows an AA′XX′ second order coupling system.

Our preliminary NMR experiments clearly show, that in addition to the potential formation of transition metal–imidazolium carbene complexes [17], the partial decomposition of the hexafluorophosphate counterion in the presence of the smallest amount of water and tin(II)chloride should be considered. (The usual work-up of the catalytic mixtures occurs very often by adding water to the ionic liquid system.)

When the [BMIM][PF_6] is exposed to moisture, two types of PF_2X_n species showing a triplet are formed (^{31}P NMR: $\delta_1 = -18.5$ ppm (br t, $^1J(^{31}P,^{19}F) = 989$ Hz); $\delta_2 = -24$ ppm (t, $^1J(^{31}P,^{19}F) = 970$ Hz). The formation of one of these species (δ_1) is supported by tin(II)chloride addition and shows species in fast equilibrium. A probable explanation of the formation of PF_2 moieties is the relatively easy substitution of equatorial fluoro ligands of PF_5 of trigonal bipiramidal structure comparing to that of apical fluoro ligands. (The detailed investigation of the formation of species containing PF_2 fragments is in progress.)

$$PtCl_2(\mathit{bdpp}) + \mathit{bdpp} + SnCl_2 \rightarrow [Pt(\mathit{bdpp})_2][SnCl_3]Cl$$

1d

Scheme 3. Formation of Pt-bis(bdpp) cation.

Therefore, it has to be noted, that *the application of ionic liquids of this type has to be done with care and ionic liquids cannot be considered as innocent solvents*.

As a conclusion it can be stated that both tin(II)chloride insertion and ligand exchange reactions take place in [BMIM][PF_6] ionic liquid analogously to those observed in conventional organic solvents like chlorinated hydrocarbons resulting in well-defined species. However, the tin(II)halide insertion depends even stronger on the platinum-ligand chelate size. (To the best of our knowledge, in spite of the widespread application of ionic liquids, this is the first NMR investigation of the elementary reactions of transition metal complexes in this novel reaction media.)

As one of the most important advantage of the above systems, the extreme stability towards oxidation has to be mentioned. (Probably one of the most important features of this system is that no phosphine dioxides and hemioxides were obtained even after exposing the samples to air for a week. From practical reasons this feature cannot be over-emphasized.) However, the decomposition of the $[PF_6]^-$ counterion in the presence of water (and tin(II)chloride) should also be considered. The aqueous work-up of the reaction mixtures might lead to serious damage both in products and catalyst.

3. Experimental

3.1. Materials

The Pt(diphosphine)Cl_2 catalytic precursors were prepared according to a known procedure [18]. The chiral bidentate ligands, bdpp*, chiraphos and prophos* were purchased from Strem and Aldrich, respectively. The ionic liquid [BMIM][PF_6] was purchased from Aldrich. Anhydrous tin(II)chloride was prepared from $SnCl_2 \times 2H_2O$ (Aldrich) by treating with 2 M equiv. of acetic anhydride and by washing with dry ether.

3.2. General

The ^{31}P and ^{13}C NMR spectra were taken on a Varian Inova 400 spectrometer operating at 161.9 and 100.6 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4. Due to the viscosity of the medium, NMR signals are much broader than those in usual deuterated solvents, introducing some uncertainty into the detection and quantification of satellite (^{195}Pt and especially ^{117,119} Sn) signals which are inherently broader than the central lines.

All operations (including preparation of complexes) were done under argon atmosphere. The appropriate complex was measured into an NMR tube, put under argon and the sufficient amount of [BMIM][PF_6] as well as the further reagents (tin(II)chloride, triphenylphosphine) were added. Locking and referencing was performed using an insert tube (2-mm o.d.) filled with D_2O.

Acknowledgements

L. K. thanks the Hungarian National Science Foundation (T035047) for the financial support and Johnson Matthey Technology Centre for the loan of platinum precursors.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071.
[2] R.T. Carlin, J.S. Wilkes, in: G. Mamantov, A. Popov (Eds.), Advances of in Nonaqueous Chemistry, VCH Publishing, New York, 1994.
[3] K.R. Seddon, Kinet. Catal. 37 (1996) 693.
[4] H. Olivier-Bourbigou, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous Phase Organometallic Catalysis: Concepts and Applications, Wiley-VCH, Weinheim, 1998.
[5] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[6] Y. Chauvin, S. Einloft, H. Olivier, Ind. Eng. Chem. Res. 34 (1995) 1149.
[7] Y. Chauvin, H. Olivier, C.N. Wyrvalski, L.C. Simon, R.F. de Souza, J. Catal. 165 (1997) 275.
[8] S. Einloft, F.K. Dietrich, R.F. de Souza, J. Dupont, Polyhedron 15 (1996) 3257.
[9] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. Dupont, Polyhedron 15 (1996) 1217.
[10] G.W. Parshall, J. Am. Chem. Soc. 94 (1972) 8716.
[11] Y. Chauvin, H. Olivier, L. Mussmann, FR 95/14,147, (1995) (Chem. Abstr. 127 (1977) P341298k).
[12] C.C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Organometallics 19 (2000) 3818.
[13] P. Wasserscheid, H. Waffenschmidt, J. Mol. Catal. A: Chemical 164 (2000) 61.
[14] I. Tóth, T. Kégl, C.J. Elsevier, L. Kollár, Inorg. Chem. 33 (1994) 5708.
[15] P.S. Pregosin, S.N. Sze, Helv. Chim. Acta 61 (1978) 1848.
[16] L. Kollár, G. Szalontai, J. Organomet. Chem. 421 (1991) 341.
[17] L.J. Xu, W.P. Chen, J.L. Xiao, Organometallics 19 (2000) 1123.
[18] L. Kollár, J. Bakos, I. Tóth, B. Heil, J. Organomet. Chem. 350 (1988) 277.