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Polyhedron 22 (2003) 3289–3292
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Synthesis of *trans*-[$RuCl_2(dppe)_2$] using the tetraalkylammonium chloride under transfer phase catalysis conditions. Crystal structure of the novel *trans*-[RuBrCl(dppe)$_2$]

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Received 23 December 2002; accepted 22 July 2003

Abstract

The catalyst precursor trans-[$RuCl_2(dppe)_2$] has been synthesized by solid state reaction of $RuCl_3 \cdot 3H_2O$ with tetrabutylammonium chloride (TBAC) and subsequent coordination with 1,2-bis-(diphenylphosphine)ethane (dppe) in dichlromethane solution. Reaction time, yield, work up and cleanness were improved by this method when compared with classical procedures. Use of tetrabutylammonium bromide (TBAB) as catalyst has afforded a novel trans-[RuBrCl(dppe)$_2$] whose crystal structure was analyzed.

Keywords: Ru(II) complex; Solid state; Ligand exchange reaction; Phase transfer catalyst

1. Introduction

Metallic complexes with polydentade phosphines as ligands have shown catalytic properties in hydrogenation and hydroformylation reactions [1]. This class of complexes has been also reported as useful catalyst precursors in cyclic olefins polymerization by metathesis (ROMP) [2].

Classical procedures for the syntheses of *trans*-[$RuCl_2(dppe)_2$] complex require of the reflux conditions in acid media [3,4] or the aqueous solution of $K_2[RuCl_5(H_2O)]$ as a precursor [5], under argon. Poor or unsatisfactory yields of complex are obtained by classical preparations.

There are some works reporting tetraalkylammonium salts as metal extractive reactants for the transference of the metal from several compounds in aqueous solutions to the organic phase [6,7]. General transport complexes could be represented by $[R_4N][Metal_m\ X_{(m+1)}L]$.

On the other hand, there are a few works relating the use of transfer phase catalysts (TPCs) in organometallic reactions involving ligand exchange [8]. Ruthenium–phosphine polyhydride complexes have been obtained using TPCs with satisfactory yield and easy work-up [9].

Here is reported the successful synthesis of *trans*-[$RuCl_2(dppe)_2$] using a solid state ligand-exchange reaction coupled with coordination through a solid–liquid transfer phase process.

The present protocol allowed us obtains the desired complex in good yield and with improved work up and cleanness when compared with classical procedure. Shortening of reaction time was also accomplished.

Extensive application of this method to preparation of a number of phosphine complexes, which are difficult under classical conditions, is under current exploration and the results will be published elsewhere.

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doi:10.1016/j.poly.2003.07.008

2. Experimental

2.1. Materials and measurements

Ruthenium trichloride trihydrate ($RuCl_3 \cdot 3H_2O$) was purchased from Aldrich, tetrabutylammonium chloride and bromide (TBAC and TBAB) were from Fluka and 1,2-bis-(diphenylphosphine)ethane (dppe) was from Sigma. Dichloromethane and diethyl ether were from Merck. The UV–Vis measurements were obtained on a Lambda 40 Perkin–Elmer spectrophotometer. The ^{31}P, ^{13}C and ^{1}H NMR spectra were registered with a Bruker AC 200 apparatus, using 85% phosphoric acid for ^{31}P and TMS as internal standard and $CDCl_3$ as solvent. EPR were registered with a Bruker ESP 300 apparatus (X-band) equipped with a TE_{102} cavity. The X-ray fluorescence spectra were registered using a VRA30 Carl Zeiss-Jena apparatus equipped with a tungsten lamp and LiF-002 as analyzer crystal. X-ray structure analyses were performed in the CAD4 Enraf Nonius diffractometer.

2.2. Synthesis of trans-[$RuCl_2(dppe)_2$] using transfer phase catalysts

Equimolar amounts (1 mmol) of $RuCl_3 \cdot 3H_2O$ (0.20 g) and TBAC (0.32 g) were previously mixed using agate mortar and pestle for 30 min. The mixture was poured into a 100 ml round-bottomed flask containing 2.1 mmol (0.88 g) of dppe previously dissolved in 50 ml of dichloromethane. The reaction was carried out for four hours with magnetic stirring at 25 ± 2 °C under argon (1 atm). Deposited product was filtered off and the filtrate was stored at 4 °C over night to recovery more precipitated product. Crude yield of complex from the first precipitation was 75% (0.76 g) as golden crystals.

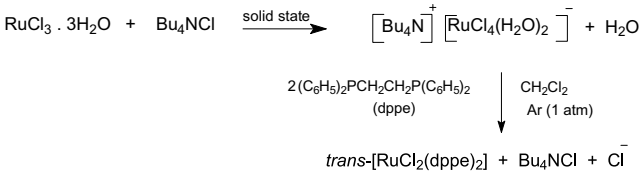
None purification was required as demonstrated by spectroscopic analysis (^{31}P,^{13}C and ^{1}H HMR) Elemental analysis: Calc.: C, 64.04; H, 4.79%. Found: C, 64.23; H, 4.96% and atomic absorption analysis: Calc.: Ru, 6.09%. Found: Ru, 6.12% were in accordance with the complex [$RuCl_2(dppe)_2$]. No traces of Ru(III) were detected from EPR analysis.

3. Results and discussion

3.1. Reaction of ruthenium chloride with tetraalkylammonium salts and dppe

Scheme 1 shows the proposed solid state reaction coupled with solid–liquid transfer phase catalysis for the synthesis of *trans*-[$RuCl_2(dppe)_2$].

The NMR spectra of crude complex were consistent with the "*trans*" configuration of [$RuCl_2(dppe)_2$] where only one signal at 44.9 ppm was observed in the ^{31}P NMR spectrum (equatorial phosphines) and five signals from



Scheme 1. Reaction pathway for the synthesis of *trans*-[$RuCl_2(dppe)_2$].

^{13}C NMR spectrum (δ ppm) at 135.6 (C ipso), 134.4 (C ortho), 128.7 (C para), 126.9 (C meta) and 29.9 (CH_2). ^{1}H NMR spectrum (δ ppm) showed signals at 7.26–6.96 (m, 40H, aromatics) and 2.73 (m, 8H, $4CH_2$), respectively.

UV–Vis spectra exhibited two electronic bands: λ_{max} 312 nm ($\epsilon = 2.7 \times 10^4$ M^{-1} cm^{-1}) and λ_{max} 448 nm ($\epsilon = 1.5 \times 10^2$ M^{-1} cm^{-1}) as expected [4].

No reaction occurred when the $RuCl_3 3H_2O$ was directly introduced into the solution containing dppe, even if catalysts (TBAC or TBAB) were added afterward. Otherwise, simultaneous addition of the ruthenium salt and catalyst, without mortar and pestle grinding was also unsuccessful. Hence, these additional experiments support the proposed solid–liquid transfer phase catalysis process and establish the importance of the previous solid stated reaction step.

Synthesis was also carried out using TBAB to verify ligand exchange. After four hours, an abundant pale yellow deposited solid was obtained and isolated (crude yield 65%). After twice crystallizations from dichloromethane/diethylether, ^{31}P NMR of product showed two close signals at 44.9 (*trans*-[$RuCl_2(dppe)_2$]) and 43.8 ppm, respectively. Intensities ratio for the two signals was around 6:1 indicating that mainly product in the mixture was the complex *trans*-[$RuCl_2(dppe)_2$]. The X-ray fluorescence spectra for the isolated minor compound established the existence of Br ($\kappa\alpha, 2\theta = 29.5°$; $\kappa\beta, 2\theta = 26.4°$) in the complex structure such as Ru and Cl, $\kappa\alpha, 2\theta = 18.0°$; $\beta, 2\theta = 15.9°$ and $\kappa\alpha, 2\theta = 65.5°$; $\kappa\beta, 2\theta = 63.2°$, respectively. Thus, the signal at 43.8 ppm was due to another phosphine complex where, presumably, one chloride ligand was substituted by bromide.

3.2. X-ray crystal structure of trans-[$RuBrCl(dppe)_2$]

The data collection for the structure of the hypothetical *trans*-[RuBrCl(dppe)$_2$] complex was performed using a single yellow crystal at room temperature. The unit cell was determined, using 25 reflections ($11.87° < \theta < 18.04°$), and the structure was solved using the WinGX system [10]. The absorption correction was made by the PSISCAN method [11] ($T_{min} = 0.88$ and $T_{max} = 0.91$). Table 1 shows the data collection and refinement conditions. Due to the disorder the system does not refine very well and Platon shows disordered solvent, but even with the application of the SQUEEZE [12] no improvement was reached.

Table 1
Crystal data and details of the structure determination for *trans*-[RuBrCl(dppe)$_2$]

Empirical formula	$C_{52}H_{48}BrClP_4Ru$
Formula weight	1013.2
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.355(2)
b (Å)	13.365(2)
c (Å)	17.156(2)
β (°)	96.28(1)
V (Å^3)	2588.0(7)
Z	2
D_{calc} (Mg m^{-3})	1.300
μ (mm^{-1})	1.282
$F(000)$	1032
Crystal size (mm)	$0.08 \times 0.10 \times 0.10$
Temperature (K)	273
Mo Kα (Å)	0.71073
θ range (°)	2.4–25.9
Dataset	$\overline{13}$: 13; 0: 16; $\overline{21}$: 0
Total unique data, R_{int}	5193, 5018, 0.057
Observed data [$I > 2.0\sigma(I)$]	2803
Nref, Npar	5018, 271
R, $wR2$, S	0.0759, 0.2483, 0.96
Minimum and maximum residual densities (e Å^{-3})	−1.91 and 1.21[a]

[a] Respectively, at 0.51 and 1.45 Å from Br $w = 1/[\sigma^2(Fo^2) + (0.1636P)^2]$, where $P = (Fo^2 + 2Fc^2)/3$.

The crystal structure determination confirmed the stoichiometry of the complex *trans*-[RuBrCl(dppe)$_2$] (Fig. 1). The structure of this complex consists of a molecule with a central Ru atoms linked to four P, one Cl and one Br atoms. The Ru atom lies on the inversion center. The Br and Cl atoms have occupation factor equal to 0.5. This kind of statistical disorder was confirmed by the solution of the structure in both $P2_1/c$ subgroups ($P2_1$ and Pc), with no increase in the refinement performance and results. Fig. 1 shows the molecule with the labeling scheme.

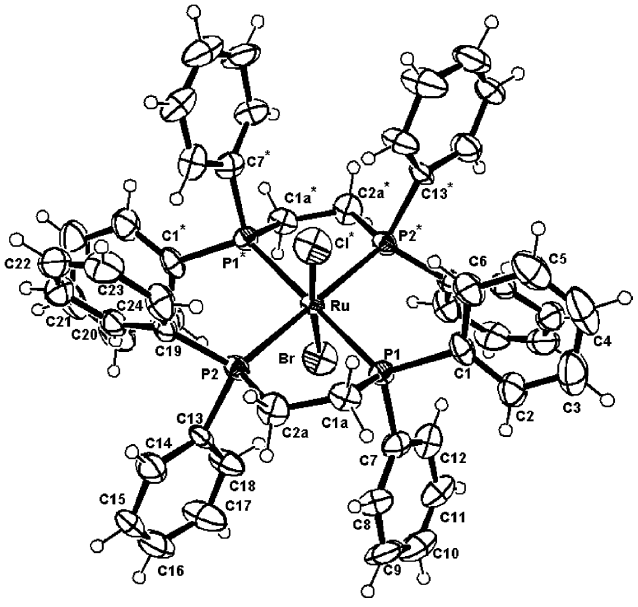


Fig. 1. ORTEP view of the *trans*-[RuBrCl(dppe)$_2$].

Table 2
Selected bond lengths (Å) and angles (°) for the *trans*-[RuBrCl(dppe)$_2$]

Bond lengths			
Ru–Br	2.49(6)	Ru–Cl	2.43(2)
Ru–P(1)	2.362(2)	Ru–P(2)	2.388(2)
P(1)–C(1)	1.880(8)	P(2)–C(2a)	1.871(9)
P(1)–C(1a)	1.842(9)	P(2)–C(13)	1.834(8)
P(1)–C(7)	1.817(9)	P(2)–C(19)	1.844(8)
Bond angles			
Br–Ru–Cl	175.8(9)	P(1)–Ru–P(2)	81.43(7)
Br–Ru–P(1)	94.0(3)	Cl–Ru–P(1)	94.1(9)
Br–Ru–P(2)	100.2(3)	Cl–Ru–P(2)	96.1(9)
P(1)–Ru–P(1*)	180	P(2)–Ru–P(2)	180
P(1)–Ru–P(2*)	98.57(7)		

In Table 2 are listed the selected bond lengths and angles. The distances in the central part of the compound are affected by the statistical disorder in the position of chloride and bromide ligands. The angle Cl–Ru–Br of 175.8(9)° is probably a consequence of the non-conventional hydrogen bonds involving the hydrogen atoms of the ethyl group located between the P atoms (dC1A-H2A1$\cdots$Br* = 3.26(2) Å; angle = 109°).

Due to its special position the Ru atom lies on the exact plane calculated for the four P atoms. The Ru–Cl distance (2.43(4) Å) compares well with the same bond in the *trans*-[RuCl$_2$(ddpe)$_2$] (2.436(1) Å) [13]. In the dppe ligand, coordinate in a bidentate fashion, the Ru–P distances are 2.362(2) and 2.388(2) Å, and have the same slight asymmetry as in the *trans*-[RuCl$_2$(ddpe)$_2$] (2.369(1) and 2.389(1) Å) [13]. In both compounds these distances are longer than those found in similar compounds.

4. Conclusions

The results described in the present work encourage us to propose the use of the solid state reaction of tetrabutylammonium chloride salts with ruthenium chloride coupled with a solid–liquid phase transfer catalysis to preparation of the *trans*-[RuCl$_2$(dppe)$_2$] as an enhanced method. A novel *trans*-[RuBrCl(dppe)$_2$] was obtained by using the bromide tetraalkylammonium salt. Hence, the use of different tetraalkylammonium salts can give new complexes by ligand exchange.

Optimization of the synthesis of *trans*-[RuBrCl(dppe)$_2$] is under investigation and studies of the catalytical activity of this complex will performed using the olefins hydrogenation as a model reaction.

5. Supplementary material

A complete set of data was deposited at the Cambridge Crystallographic Data Centre with number CCDC 193000. Copies of this information may be

obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors are gratefully to Professor Douglas Wagner Franco by useful suggestions and discussions and to Mrs Vania Cardoso Fernandes by X-ray fluorescence analysis. We are also thankful to CAPES, CNPq and FAPESP for financial support.

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