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REGENERATION OF PLATINUM-METAL-BASED CATALYSTS WITH CARBOXYPHOSPHINES AS EXTRACTANTS

Alexandr JEGOROV and Jaroslav PODLAHA

South Bohemian Biological Centre, Czechoslovak Academy of Sciences, Branišovská 31, 370 05 České Budějovice and Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czechoslovakia

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Separation of platinum-metal-based homogeneous catalysts was achieved by their conversion to complexes of functionalized phosphines of the general formulae $R_{3-n}P[(CH_2)_x CO_2H)]_n$, R = Me, Et, Ph, $n = 1, 2, 3$, $x = 1, 2$, and $[(HO_2CCH_2)PCH_2]_2$, followed by extraction of the complexes into aqueous phase. This approach to regeneration of platinum metals from reaction mixtures after carrying out homogeneously catalyzed reactions was demonstrated on 11 examples of various types of reactions with Ru, Rh, Pd, Os, Ir and Pt compounds as catalysts.

Keywords: Complexes of platinum metals, homogeneous catalysis, regeneration of platinum metals, carboxyphosphines

1. Introduction

In recent years, considerable effort has been devoted to the preparation of water-soluble complexes of platinum metals. Representative complexes have been described with quarternary-amino [1] or sulphonated [2] phospines as ligands. The complexes are susceptible, at least in principle, of extraction into the aqueous phase or of catalysis in two-phase systems. This property already led to industrial applications, e.g., in regeneration of nickel complexes used in oligomerization of ethylene [3] (Shell Higher Olefin Process). The need of separation and regeneration of platinum metal catalysts is in fact the greatest disadvantage of homogeneous catalysis, which is, on the other hand, usually more selective and works at milder conditions than heterogeneous catalysis [4].

In this paper we demonstrate a different approach to the regeneration of platinum-metal-based homogeneous catalysts, the principle of which consists in the conversion of the catalyst to a water soluble complex of carboxyphosphine followed by its extraction with water after completion of the catalytic reaction [5].

Table 1
Examples of extraction of platinum-metal-based catalysts with carboxyphosphines

Catalyst	Reaction (solvent)	Ligand and procedure [a]	Separation of metal (%) ($c_{aq.}/c_{org.}$) [ppm] [b]
$RhCl(PPh_3)_3$	hydrogenation of cyclohexene (benzene) [32]	$PhP(CH_2CO_2H)_2$ sample + EtOH + 0.5 M Na_2CO_3, 1 : 1 : 1 [d]	86.5% (56.1/15.8)
		$H_4L \cdot 2HBr$ [g] sample + EtOH + 0.1 M Na_2CO_3, 1 : 1 : 1 [e]	93.0% (71.2/10.6)
$RhH(CO)(PPh_3)_3$	hydroformylation of octene (toluene) [33]	$P(CH_2CH_2CO_2H)_3 \cdot HCl$ sample + EtOH + 0.5 M Na_2CO_3, 1 : 1 : 1 [d]	92.4% [c] (130 and 431/25.6)
		$H_4L \cdot 2HBr$ [g] sample + EtOH + 0.5 M Na_2CO_3, 1 : 1 : 1 [d]	95.5% [c] (138 and 1350/15.7)
		$PhP(CH_2CO_2H)_2$ sample + EtOH + 0.5 M Na_2CO_3, 1 : 1 : 1 [d]	90.8% [c] (12 and 204/36.5)
$[Rh(C_2H_4)_2Cl]_2$	oxidation of styrene (tetraline) [34]	$PhP(CH_2CO_2Na)_2$ sample + 0.1 M Na_2CO_3, 1 : 1 [f]	97.9% (111/2.4)
$IrCl(CO)(PPh_3)_2$	hydrosilylation of ethanol (benzene) [35]	$EtP(CH_2CO_2Na)_2$ sample + H_2O, 1 : 1	95.8% (468/24.3)
$(NEt_4)_2Pd_2Cl_6$	oligomerisation of allyl chloride (dichloromethane) [36]	$P(CH_2CO_2Na)_3$ sample + H_2O, 1 : 1	97.9% (9387/234)
$PdCl_2(PhCN)_2$	addition of phenylacetylene to allyl chloride (allyl chloride) [36]	$MeP(CH_2CO_2H)_2 \cdot HCl$ sample + 0.5 M Na_2CO_3, 1 : 1	99.0% (5530/52)
	isomerisation of 1-pentene (benzene) [37]	Na_4L [g] sample + H_2O, 1 : 1	96.5% (157/51.7)
		$Ph_2PCH_2CO_2Na$ sample + EtOH + H_2O, 1 : 1 : 1	99.0% [h] (157/51.7) (22/4.4) [h]
$[Pt(C_2H_4)_2Cl]_2$	reaction of tetrahydropyrane with acetyl chloride (THP) [38]	$PhP(CH_2CO_2H)_2$ sample + 0.5 M Na_2CO_3, 1 : 1	99.5% (4650/25.6)
$[Pt(C_2H_4)_2Cl]_2$	hydrosilylation of 1-hexene (1,2-dichlorethane [39]	$H_4L \cdot 2HBr$ [g] sample + EtOH + 0.1 M Na_2CO_3, 1 : 1 : 1 [d]	98.0% (120/4.8)
		$PhP(CH_2CO_2H)_2$ sample + EtOH + 0.1 M Na_2CO_3, 1 : 1 : 1 [d]	97.0% (117/6.8)

Table 1 (continued)

Catalyst	Reaction (solvent)	Ligand and procedure [a]	Separation of metal (%) ($c_{aq.}/c_{org.}$) [ppm] [b]
$RuCl_2(PPh_3)_3$	chloro-trichloromethylation	$PhP(CH_2CO_2H)_2$	88.3%
	of cyclooctene (benzene) [40]	sample + EtOH + 0.1 M Na_2CO_3, 1:1:1 [d]	(147/31.5)
		$MeP(CH_2CO_2H)_2 \cdot HCl$	96.3%
		sample + EtOH + 0.1 M Na_2CO_3, 1:1:1	(194/12.4)
		$H_4L \cdot 2HBr$ [g]	94.5%
		sample + EtOH + 0.1 M Na_2CO_3, 1:1:1	(172/16.7)
$OsBrH(CO)(PPh_3)_3$	isomerisation of 1-hexene (toluene) [41]	$PhP(CH_2CO_2H)_2$	95.4%
		sample + EtOH + 0.1 M Na_2CO_3, 1:1:1	(257/32.7)

[a] Molar ratio metal:phosphorus = 1:4 was used in all cases, mixture was shaken for 3 min at ambient temperature unless otherwise noted;

[b] Calculation of the transfer into aqueous phase (%) was based on total amount of the metal in aqueous ($c_{aq.}$) and organic ($c_{org.}$) phases and their volumes;

[c] three-phase system with two aqueous layers;

[d] phosphine was added before mixing with water and the mixture was heated: 70 °, 1 min;

[e] 70 °, 5 min;

[f] 100 °, 3 min;

[g] $H_4L = (HO_2CH_2)_2P(CH_2)_2P(CH_2CO_2H)_2$;

[h] after repeated extraction with fresh extractant.

2. Experimental

CHEMICALS

Phosphines and platinum metal compounds were prepared by known methods: $Ph_{3-n}P(CH_2CO_2H)_n$, $n = 1$ [6], 2 [7], 3 [8], $RP(CH_2CO_2H)_2$, R = Me [9], Et [10], $P[(CH_2)_2CO_2H)_3$ [11], $[(HO_2CCH_2)PCH_2]_2$ [12], $RhH(CO)(PPh_3)_2$ [13], $RhCl(PPh_3)_2$ [14], $[Rh(C_2H_4)_2Cl]_2$ [15], $IrCl(CO)(PPh_3)_2$ [16], $(NEt_4)_2Pd_2Cl_6$ [17], $PdCl_2(PhCN)_2$ [18], $[Pt(C_2H_4)_2Cl]_2$ [19], $RuCl_2(PPh_3)_3$ [20] and $OsBrH(PPh_3)_3$ [21]. Catalysis was carried out exactly as described in the original literature (Table 1), the composition and yields of the products were always checked by appropriate methods [IR (Perkin-Elmer 684), GLC (Chrom 31), ^1H NMR (Tesla BS 687A, 80 MHz)].

ANALYSIS

Platinum metals were determined photometrically on a VSU-2 instrument (K. Zeiss, Jena, GDR) by the following methods: Rh [22], wet ashing with conc. H_2SO_4, ($\varepsilon_{427} = 2.9 \cdot 10^4$); Pd [23], wet ashing with a mixture of 36% HCl and 65%

HNO_3 (3 : 1, v/v), ($\varepsilon_{308} = 2.4 \cdot 10^4$); Pt [24], wet ashing with a mixture of 65% HNO_3 and 70% $HClO_4$ (5 : 1, v/v), ($\varepsilon_{403} = 7.8 \cdot 10^3$); Ru [25], samples were evaporated to dryness with 0.15 g KOH and 0.25 g KNO_3 and then melted for 5 min at ca 1200 ° C and dissolved in water, ($\varepsilon_{470} = 1.7 \cdot 10^3$); Os [26], samples were evaporated with 5 ml of 0.1 M NaOH in methanol and melted with 2 g of a mixture of KNO_3 and Na_2CO_3 (1 : 1, w/w); ($\varepsilon_{480} = 4.8 \cdot 10^3$); a new method was developed for Ir: samples were mineralized with a mixture of conc. H_2SO_4 and 70% $HClO_4$ (3 : 1, v/v) in a Kjeldahl flasks, evaporated to dryness, redissolved in conc. H_2SO_4 and the absorbance was measured against conc. H_2SO_4, ($\varepsilon_{308} = 2.4 \cdot 10^4$). Calibration of photometric methods was based either on gravimetric determination of pure inoganic salts (Rh, Pd and Pt) or on mineralization of recrystallized complexes ($IrCl(CO)(PPh_3)_2$, $RuCl_2(PPh_3)_3$ and $(NH_4)_2OsBr_6$).

EXTRACTION PROCEDURE

Fourfold molar equivalent of phosphorus (with respect to the platinum metal) was added in the form of either the free acid, the hydrohalide or the sodium salt, to one volume of the reaction mixture together with 1–2 volumes of water or an aqueous buffer solution. The two-phase mixture was stirred vigorously for 3 min and phases were then separated. The amount of each phase was determined and aliquots were taken for analysis.

3. Results and discussion

The results are summarized in table 1 correspond to a single partition, the yield can be in most cases improved by repetition of the extraction process. The carboxyphosphine complexes are formed by reaction of the catalyst with phosphines, the reaction being usually complete within several minutes at room temperature; in the case of kinetically inert complexes, e.g. those of iridium, heating is necessary.

A number of complexes of free carboxyphosphine acids, e.g. of Rh [27,28], Ru [29], Pd [30] and Pt [31] with diphenylphosphinoacetic acid, were already synthesized and characterized. In contrast, platinum-metal complexes of phosphines bearing two or more carboxy groups are practically unknown so far. Likewise the complexes of salts of phosphineacetic acids were not reported yet, probably due to their high solubility in water and pronounced tendency to form intractable oils.

The prominent feature of chemistry of carboxyphosphines consists in the formation of thermodynamically very stable P, O-chelates, either by simple proton abstraction and then coordination or via oxidative addition of the carboxyl group [28]. Consequently, carboxyphosphines are advantageous in that they are capable to substitute P-monodentate tertiary phosphines as well as other ligands commonly acting in homogeneous catalysis. The second factor which must be taken into account in designing a reagent for extraction is a delicate balance of solubilities of the ligands and their complexes in the two phases. Fortunately, this property can be effectively tuned by the COO/P ratio and by the type of R-substituent of the particular ligand. Since the chelation consumes one hydrophilic group, the extraction is best achieved with the phosphines bearing two carboxy groups per one phosphorus atom. Phospines with more carboxyl functions are usually too insoluble in the organic phase to enable an efficient contact between the catalyst and phospine.

This method of separation of platinum metals from catalytic mixtures proceeds under considerably milder conditions than, e.g., their extraction with strong inorganic acids. Hence, we belive that it could find use in the cases where the reaction products would tend to be sensitive to more drastic separation methods.

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