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Synthesis of PEG–iridium conjugates and their use as hydrogenation catalysts in a water/substrate two-phase medium

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Abstract

New syntheses of PEG-$(OCH_2C_5H_4N)_2$ and PEG-$(OC_6H_4PPh_2)_2$ (PEG: poly(ethylene glycol)) conjugates are reported. An iridium hydrogenation catalyst **1**, is shown to catalyze hydrogenation in a water/substrate two-phase system. Attachment of **1** to PEG to make **2** and **3** succeeds in making the complex water-soluble and allows it to retain some of its catalytic ability, but leads to micelle formation that inhibits the separation of organic and aqueous phases. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the rise of 'green chemistry' there is increased emphasis both on homogeneous catalysis and on ways to avoid organic solvents in catalytic reactions [1]. In water/organic two-phase systems, water soluble catalysts do work, but can give low turnover frequencies (TOF). Dror considers cosolvents necessary for acceptable hydrogenation rates [2]. Slow diffusion of substrate into the water phase is considered to be the main problem. Rhône Poulenc have reported a successful substrate/water two-phase hydrogenation without cosolvents, using ruthenium and rhodium Tris(*m*-sulfonatophenyl)phosphine complexes [3,4].

Our cationic iridium hydrogenation catalysts of type $[(cod)Ir(PR_3)py]PF_6$ may have advantages for this application. They are water-stable and have high activity. Although the precursors have no significant water solubility, they can form aqua complexes as intermediates and, thus, become somewhat water soluble during turnover. Some stable aqua complexes of this type have been isolated (e.g. $[(H_2O)_2IrH_2(PR_3)_2]PF_6$) and even structurally characterized. These aqua species not only have enhanced water-solubility, but can undergo deprotonation to give neutral, potentially organic-soluble species. For simplicity and comparability, we used $[(cod)Ir(PPh_3)py]PF_6$ (**1**) or its PEG-bound equivalents throughout.

Water-solubilization of a metal complex can often be achieved by attachment to a water-soluble polymer [5–7]. Poly(ethylene glycol) (PEG) is commonly used because of its solubility properties; it is soluble in water and some organic solvents, e.g. CH_2Cl_2 and DMF, but can be precipitated with other organic solvents, e.g. Et_2O and hexane [8,9]. These solubility properties potentially allow PEG-based catalysts to undergo phase transfer, which is in turn expected to give improved catalytic activity in two-phase systems.

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2. Experimental

Unless otherwise noted, all manipulations were conducted under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were dried by common procedures. Water was deoxygenated by purging with nitrogen for 30 min. (cod)IrCl(PPh_3) and [(cod)Ir($py)_2$]PF_6 were prepared according to literature procedures [10,11]. All other reagents were purchased from Aldrich and used without further purification. NaH was a 60% weight dispersion in mineral oil. All PEG-derived polymers were stored under nitrogen in the dark. NMR spectra were recorded in CD_2Cl_2 on a GE Omega 300 MHz spectrometer. ^{31}P-NMR chemical shifts were referenced to an external standard (85% H_3PO_4). GC/MS analyses were made on a HP-5971A MSD interfaced to a HP-5890 Series II GC with a fused silica capillary column.

2.1. Preparation of PEG-($OC_6H_4PPh_2)_2$

We have prepared this material by three different routes. The term PEG-X_2 implies that the X group is present at both ends of the linear PEG polymer.

2.1.1. Mitsunobu procedure via PEG-($OC_6H_4I)_2$

The first Mitsunobu step is based on a procedure described by Bittner and Assaf [12]. A mixture of PEG-3400 (5.0 g, ca. 1.5 mmol), *p*-iodophenol (1.0 g, 4.5 mmol), PPh_3 (1.4 g, 5.4 mmol), and diethyl azodicarboxylate (0.85 ml, 5.4 mmol) in dry CH_2Cl_2 (40 ml) was stirred at room temperature for 12 h. The yellow solution was concentrated to ca. 15 ml and added dropwise to Et_2O (ca. 200 ml). The white precipitate (PEG-($OC_6H_4I)_2$) that formed was filtered (medium frit), washed with Et_2O (3 × 20 ml), and dried. Yield = 95%. ^{1}H-NMR: 7.54 (d, C_6H_4), 6.70 (d, C_6H_4), 3.58 (m, PEG CH_2).

The second step follows a coupling strategy by Stelzer [13]. To a solution of PEG-($OC_6H_4I)_2$ (2.5 g, ca. 0.66 mmol) in acetonitrile (35 ml) was added NEt_3 (0.25 ml, 1.8 mmol), $Pd(OAc)_2$ (2 mg, 8.9 μmol), and $HPPh_2$ (0.31 ml, 1.8 mmol). The mixture was heated to 45°C for 12 h and then at 80°C for another 12 h. After cooling, the resulting red solution was added dropwise to degassed Et_2O. The white precipitate was filtered, washed three times with degassed Et_2O, three times with degassed *i*PrOH, and dried in vacuo. Yield = 95%. ^{1}H-NMR: 7.30 (m, Ar), 6.93 (d, Ar), 4.13 (α CH_2 PEG), 3.58 (m, PEG CH_2). ^{31}P-NMR: −6.7 ($Ph_2PC_6H_4$). No starting material was present (NMR).

2.1.2. Mitsunobu procedure via 4-iodophenol

p-Hydroxyphenyldiphenyl phosphine (prepared according to [13]) was attached to PEG-3400 by the Mitsunobu procedure described above. Yield = 95%. The ^{1}H and ^{31}P-NMR data were identical to those reported above.

2.1.3. Substitution procedure via PEG-($OTs)_2$

To a cooled (ice bath) solution of PEG-3400 (50 g, ca. 15 mmol) in CH_2Cl_2 (100 ml), was added *p*-toluenesulfonyl chloride (11.5 g, 60 mmol) and pyridine (10 ml, 120 mmol) with stirring. The solution was allowed to warm to room temperature and stirring was continued for 24 h. The solution was then concentrated to ca. 60 ml and added dropwise to Et_2O (ca. 600 ml). The white precipitate was filtered and washed three times with Et_2O (3 × 50 ml). The dried solid was suspended in toluene (500 ml). The mixture was filtered and the filtrate evaporated. The residue was dissolved in CH_2Cl_2 (50 ml) and the solution was added dropwise to Et_2O. The PEG-($OTs)_2$ that precipitated was filtered, washed with Et_2O, and dried in vacuo. Yield = 85%. ^{1}H-NMR: 7.76 (d, C_6H_4), 7.35 (d, C_6H_4), 3.58 (m, PEG CH_2), 2.43 (s, CH_3).

To a solution of *p*-hydroxyphenyldiphenyl phosphine [13] (0.6 g, 2.2 mmol) in CH_2Cl_2 (10 ml) was added NaH (0.1 g, 2.4 mmol). After stirring for 10 min, the suspension was filtered and the filtrate was added to a solution of PEG-($OTs)_2$ (3.7 g, ca. 1.0 mmol) in CH_2Cl_2 (30 ml). After stirring for 12 h, the solvent was evaporated. Toluene (100 ml) was added to the residue and the mixture was stirred for 30 min. The mixture was filtered and the filtrate evaporated to leave a residue that was then dissolved in CH_2Cl_2. This solution was added dropwise to Et_2O. The precipitated solid was filtered, washed with Et_2O, and dried in vacuo. Yield = 95%. The ^{1}H and ^{31}P-NMR data were identical to that reported above. Seventy six percent conversion to PEG-($OC_6H_4PPh_2)_2$ as determined by comparison of PEG-($OTs)_2$ C_6H_4 doublet at 7.8 ppm to PEG-($OC_6H_4PPh_2)_2$ C_6H_4 doublet at 6.93 ppm.

2.2. Preparation of PEG-($OCH_2C_5H_4N$)$_2$

To a solution of 4-pyridylcarbinol (0.55 g, 5.0 mmol) in DMF (30 ml), was added NaH (0.16 g, 4.1 mmol). After stirring for 1 h, the resulting red solution was added slowly to a solution of PEG-(OTs)$_2$ (3.40 g, ca. 1.0 mmol) in DMF (30 ml). After stirring for 12 h at room temperature, water (20 ml) was added while the reaction mixture was cooled with an ice bath. The mixture was first extracted with Et_2O and then with CH_2Cl_2. Only the CH_2Cl_2 extracts were collected. The CH_2Cl_2 extracts were concentrated to ca. 15 ml and added dropwise to Et_2O. The white solid was filtered, washed with Et_2O, and dried. Yield = 95%. ^{1}H-NMR: 8.52 (d, py), 7.26 (d, py), 4.56 (s, CH_2), 3.59 (m, PEG CH_2). No impurities observable by NMR.

2.3. Preparation of PEG-($OC_6H_4PPh_2$)$_2$–iridium conjugate **2**

To a solution of [(cod)Ir(py)$_2$]PF_6 (0.10 g, 0.18 mmol) in CH_2Cl_2 (2 ml) was added a solution of PEG-($OC_6H_4PPh_2$)$_2$ (0.31 g, ca. 0.08 mmol) in CH_2Cl_2 (5 ml). The orange solution was stirred for 30 min and then concentrated to 2 ml. The solution was filtered and the filtrate was added dropwise to Et_2O (20 ml). The orange solid was filtered and dried in vacuo. Yield = 95%. ^{1}H-NMR: 8.22 (py), 7.43 (Ar), 7.21 (py), 7.08 (C_6H_4O), 4.44 (m, vinyl cod), 3.60 (m, PEG CH_2), 2.5–1.9 (allyl cod). ^{31}P-NMR: 16.6 (s, $Ph_2PC_6H_4$), −143.9 (septet, PF_6^-). No impurities observable by NMR except doublet at 8.64 ppm from [(cod)Ir(py)$_2$]PF_6 py. Eighty-five percent conversion determined by comparison of product doublet at 8.22 ppm to [(cod)Ir(py)$_2$]PF_6 doublet at 8.64 ppm.

2.4. Preparation of PEG-($OCH_2C_5H_4N$)$_2$–iridium conjugate **3**

To a solution of $AgPF_6$ (0.09 g, 0.36 mmol) in acetone (3 ml) was added slowly a solution of (cod)IrCl(PPh_3) (0.22 g, 0.37 mmol) in acetone (15 ml). After stirring for 5 min, the mixture was filtered and the filtrate was added to a solution of PEG-($OCH_2C_5H_4N$)$_2$ (0.5 g, ca. 0.15 mmol) in CH_2Cl_2. This mixture was stirred at room temperature for 1 h. The solvent was evaporated and CH_2Cl_2 (20 ml) was added. The solution was filtered through celite and the filtrate was concentrated to 5 ml. The red solution was added dropwise to Et_2O. The orange red solid was filtered and dried in vacuo. Yield = 95%. ^{1}H-NMR: 8.14 (d, py), 7.48 (m, Ph), 7.14 (d, py), 4.47 (m, vinyl cod), 4.40 (s, CH_2), 3.60 (m, PEG CH_2), 2.4–1.7 (allyl cod). ^{31}P-NMR: 17.5 (s, Ph_3P), −144.0 (septet, PF_6^-). No impurities observable by NMR.

2.5. Typical hydrogenation procedure

The PEG–iridium conjugate (0.092 g, 18 μmol, 0.5 mol.%) was dissolved in water (5 ml) under N_2 in a 50 ml Schlenk flask equipped with a septum. Allylbenzene (1 ml, 7.5 mmol) was added and the mixture was stirred vigorously, while H_2 (1 atm) was bubbled via a septum. The H_2 outlet needle was removed after the flask had filled with H_2. The progress of the reaction was followed by removing 0.1 ml of the organic layer after fixed times with a syringe, extracting with Et_2O, and analyzing by GC/MS.

3. Results and discussion

PEG-($OC_6H_4PPh_2$)$_2$ has previously been synthesized by Wentworth and Janda [14] and by Kim [15]. The Wentworth–Janda procedure requires protection and deprotection steps for the synthesis of *p*-hydroxyphenyldiphenylphosphine. PEG-3400 is converted to its methanesulfonyl derivative and then coupled to *p*-hydroxyphenyldiphenylphosphine. Five steps are needed in total. Kim reports a one-pot method of synthesizing PEG-($OC_6H_4PPh_2$)$_2$ from PEG-3400 via deprotonation of PEG with K/naphthalene and addition of (4-bromophenyl)diphenylphosphine, but significant phosphine oxidation occurs during isolation.

Soluble, polymer-bound phosphines have been synthesized recently for use in fluorous [16], two-phase organic [17], and aqueous [18] systems. The phosphines of all of these polymers, however, are alkyldiphenylphosphines; their electronics differ appreciably from triphenylphosphine.

We have developed three high-yield procedures for the synthesis of high-purity PEG-($OC_6H_4PPh_2$)$_2$ which require only two or three steps. Method 1, shown in Eq. (1), begins with a Mitsunobu reaction between PEG-3400 and *p*-iodophenol, followed by a Pd-catalyzed coupling between the resulting PEG-(OC_6H_4I)$_2$ and diphenylphosphine. When, the

coupling reaction was stopped after only 5 h of heating at 80°C, C_6H_4 protons from the *p*-iodophenol starting material were still present (^{1}H-NMR resonances at 7.54 and 6.70 ppm). Heating at 80°C for an additional 7 h gives a product having a spectrum with PEG-$(OC_6H_4PPh_2)_2$ aromatic protons only (7.30 and 6.93 ppm). The α-methylene PEG protons (PEG-$(OCH_2CH_2OC_6H_4PPh_2)_2$) are also seen (4.13 ppm) along with the intense PEG methylene resonance (3.58 ppm). The ^{31}P-NMR spectrum shows no evidence of phosphine oxide. The second method is identical except for the order of the Mitsunobu and P-aryl coupling steps (Eq. (2)). Both methods require only two steps.

$$\text{PEG-(OH)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{IC}_6\text{H}_4\text{OH, PPh}_3\text{/DEAD}} \text{PEG-(OC}_6\text{H}_4\text{I)}_2 \xrightarrow[\text{MeCN}]{\text{HPPh}_2, \text{Pd(OAc)}_2, \text{NEt}_3} \text{PEG-(OC}_6\text{H}_4\text{PPh}_2)_2 \quad (1)$$

$$\text{IC}_6\text{H}_4\text{OH} \xrightarrow[\text{MeCN, NEt}_3]{\text{HPPh}_2, \text{Pd(OAc)}_2} \text{HOC}_6\text{H}_4\text{PPh}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{PEG-(OH)}_2, \text{PPh}_3\text{/DEAD}} \text{PEG-(OC}_6\text{H}_4\text{PPh}_2)_2 \quad (2)$$

The third method (Eq. (3)) requires two steps from $HOC_6H_4PPh_2$, which must be synthesized via Eq. (2). The product shows evidence of PEG-$(OTs)_2$ starting material in the PEG-$(OC_6H_4PPh_2)_2$ ^{1}H-NMR at 7.8 ppm, but gives the ^{1}H-NMR with the fewest spectroscopically apparent impurities. PEG-$(OTs)_2$ is formed from the reaction between PEG-3400, *p*-toluenesulfonyl chloride, and pyridine. PEG-$(OC_6H_4PPh_2)_2$ is then made by the reaction of PEG-$(OTs)_2$ with the sodium salt of *p*-hydroxyphenyldiphenylphosphine. The product NMR data from all three of our methods are consistent with those reported in [14].

$$\text{PEG-(OH)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{p\text{-TsCl/py}} \text{PEG-(OTs)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{HOC}_6\text{H}_4\text{PPh}_2, \text{NaH}} \text{PEG-(OC}_6\text{H}_4\text{PPh}_2)_2 \quad (3)$$

The reaction between $[(cod)Ir(py)_2]PF_6$ and PR_3 has been studied extensively. In the presence of one equivalent of PR_3, $[(cod)Ir(py)_2]PF_6$ undergoes substitution to give $[(cod)Ir(PR_3)py]PF_6$ (Eq. (4)) [10]. The cod allyl and vinyl protons are no longer equivalent causing extra resonances to appear in the ^{1}H-NMR. A color change from yellow to red–orange is observed.

$$[(\text{cod})\text{Ir(py)}_2]\text{PF}_6 \xrightarrow[\text{acetone/EtOH}]{\text{PR}_3} [(\text{cod})\text{Ir(PR}_3\text{)py}]\text{PF}_6 \quad (4)$$

By analogy with the chemistry of Eq. (4), PEG-$(OC_6H_4PPh_2)_2$ can be combined with $[(cod)Ir(py)_2]PF_6$ to give **2**. The ^{1}H-NMR spectrum of the product does indeed show the same aromatic and cod peaks found for $[(cod)Ir(PPh_3)py]PF_6$, but it also shows free $[(cod)Ir(py)_2]PF_6$ (the extra 12.5% that was in excess of stoichiometric ratio plus 15% that did not react) is precipitated along with **2** ($[(cod)Ir(py)_2]PF_6$ py resonance at 8.64 ppm). This should not affect catalysis, though, because it has been shown that $[(cod)Ir(py)_2]PF_6$ is ineffective as a hydrogenation catalyst [19]. The ^{31}P-NMR spectrum shows only peaks at 16.6 ppm for the phosphine bound to iridium and −143.9 ppm for the PF_6^- anion; no phosphine oxide resonance is observed.

PEG-$(OCH_2C_5H_4N)_2$ was prepared from a substitution reaction between PEG-$(OTs)_2$ and the sodium salt of 4-pyridylcarbinol (Eq. (5)). This is the same approach used in the third method of the synthesis of PEG-$(OC_6H_4PPh_2)_2$ (Eq. (3)).

$$\text{PEG-(OH)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{p\text{-TsCl/py}} \text{PEG-(OTs)}_2 \xrightarrow[\text{DMF}]{\text{HOCH}_2\text{C}_5\text{H}_4\text{N, NaH}} \text{PEG-(OCH}_2\text{C}_5\text{H}_4\text{N)}_2 \quad (5)$$

It is known that in the presence of an excess of pyridine and a PF_6^- salt, (cod)IrCl(PR_3) will undergo substitution and counterion exchange to give $[(cod)Ir(PR_3)py]PF_6$ (Eq. (6)) [10]. Use of $AgPF_6$ facilitates the reaction because Ag precipitates the chloride.

$$(\text{cod})\text{IrCl(PR}_3) \xrightarrow[\text{MeOH}]{\text{excess py, AgPF}_6} [(\text{cod})\text{Ir(PR}_3\text{)py}]\text{PF}_6 \quad (6)$$

To prepare **3**, (cod)IrCl(PPh_3) is treated with $AgPF_6$ in acetone which serves to activate it by conversion to [(cod)Ir(acetone)(PPh_3)]PF_6 in which the acetone is a much better leaving group than the original chloride. The acetone could then be replaced by the pyridine of PEG-($OCH_2C_5H_4N)_2$. The PEG bound pyridine is not in excess as Eq. (6); this is probably, why conversion to the intermediate acetone complex is needed in the PEG case. The py peaks in the ^{1}H-NMR shift upfield indicating coordination of Ir and no py peaks from uncoordinated PEG-($OCH_2C_5H_4N)_2$ remain.

Complexes of type [(cod)Ir(PR_3)py]PF_6 are known to be excellent hydrogenation catalysts in CH_2Cl_2, especially, where R = cyclohexyl or isopropyl [19,20]. Upon addition of H_2, cod is hydrogenated and lost leaving active sites for hydrogen to oxidatively add and for substrate to bind. Turnover frequencies of 6400 (mol reduced product/mol catalyst × h) can be achieved with 1-hexene.

1–3 were tested for hydrogenation activity in a water/allylbenzene two-phase system. Use of allylbenzene as a substrate allowed hydrogenation and isomerization to be monitored. Aliquots of the organic layer were removed every 30 min for 2.5 h, extracted with ether, and analyzed by GC/MS to determine product ratios.

As shown in Table 1(b), **1** hydrogenates allylbenzene in a water/substrate two-phase medium with a maximum TOF of 62 h^{-1}. This can be compared with a conventional hydrogenation in CH_2Cl_2 which gives

Table 1
One- and two-phase hydrogenation of allylbenzene with 0.5 mol% [(cod)Ir(PPh_3)py]PF_6-based catalysts[a]

Reaction time (min)					TOF	Total TOF
(a) [(cod)Ir(PPh_3)py]PF_6 (**1**), no PEG, CH_2Cl_2 as solvent, one-phase						
5	92.0	3.9	4.1	0	89	181
30	24.3	50.0	22.5	3.3	187	284
60[b]	0	80.0	20.0	0	150	188
(b) [(cod)Ir(PPh_3)py]PF_6 (**1**), no PEG, water as solvent						
30	95.6	4.4	0	0	17	17
60	62.5	32.8	4.7	0	62	70
90	36.2	46.8	14.9	2.1	59	80
120	18.5	54.4	22.9	4.1	51	76
150	8.1	67.2	21.8	2.9	50	69
(c) [(cod)Ir(PPh_3)py]PF_6 (**1**), PEG-3400, water as solvent						
30	97.1	2.9	0	0	11	11
60	64.5	26.6	7.7	1.2	50	67
90	42.5	39.8	15.0	2.7	50	72
120	32.3	49.7	15.0	3.1	47	64
150	30.0	49.5	17.5	3.0	37	53
(d) PEG/PPh_3 iridium catalyst **2**, water as solvent						
30	89.2	6.2	4.6	0	23	41
60	77.6	12.0	10.4	0	23	42
90	70.9	14.8	14.3	0	19	36
120	57.8	24.1	18.1	0	23	40
150	54.3	29.7	16.0	0	22	34
(e) PEG/Py iridium catalyst **3**, water as solvent						
30	0	0	0	0	0	0
60	90.6	9.4	0	0	18	18
90	77.5	13.2	9.3	0	17	28
120	54.9	22.3	22.7	0	21	42
150	51.3	20.9	27.8	0	16	37

[a] Yields (%) determined by GC/MS. TOF: [mol propylbenzene/(mol cata)(h)]. Total TOF: [mol propylbenzene + mol isomerized products/(mol cata)(h)].

[b] No significant further changes occur after 60 min.

a TOF of 187 h^{-1} (Table 1(a)). The fact that **1** does not dissolve appreciably in water does not inhibit catalysis and only increases the amount of time needed for at least 92% hydrogenation/isomerization by 90 min.

Considering the possible presence of protonation/deprotonation equilibria, we looked at the effect of running the catalysis in the presence of either *p*-TsOH or $N(CH_2CH_2OH)_3$. The presence of acid or base did not seem to affect catalysis rates, implying that protonation/deprotonation is not critical.

Addition of PEG-3400 to the two-phase system causes the maximum TOF to drop to 50 h^{-1} (Table 1(c)). The water layer takes on a cloudy appearance. Although PEG is soluble in water, salt trapped in the PEG can cause PEG precipitation and micelle formation.

2 and **3** were less active still than the noncovalently linked **1**/PEG mixed system with maximum TOFs of 23 and 21 h^{-1} respectively (Table 1(d) and (e)). The micelle formation problem is worsened with **2** and **3** because the iridium complexes themselves are salts. The extent of micelle formation in the reaction mixture when **2** or **3** were used made separation of organic and aqueous layers impossible.

Conjugate **2** was more active than **3**, and also appeared to be more stable with time, even though the two are essentially identical except for the point of attachment of the PEG. Presumably, the PEG-$(OC_6H_4PPh_2)_2$ ligand binds best and retains the metal in the conjugate, while the Ir–N bond can dissociate.

4. Conclusion

We have described an improved synthesis of PEG-$(OC_6H_4PPh_2)_2$ and syntheses of PEG-$(OCH_2C_5H_4N)_2$ and PEG–Ir conjugates of types **2** and **3**. We have also shown that catalyst **1** is suitable for two-phase operation in a water/substrate mixture and that **2** and **3** possess limited hydrogenation activity.

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