Platinum(II) Diphosphinamine Complexes for the Efficient Hydration of Alkynes in Micellar Media

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Received: April 27, 2011; Revised: December 12, 2011; Published online: April 12, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201100326.

Abstract: Highly active monomeric bis-cationic platinum(II) catalysts bearing small bite angle diphosphinamine [N,N-bis(diarylphosphino)amine] 'PNP' ligands efficiently catalyze Markovnikov hydration of terminal and internal alkynes to the corresponding ketones in water. Catalyst solubilization in water is achieved *via* ion pairing with anionic micelles formed by surfactant addition. The micelles ensure dissolution of apolar alkynes and promote the intimate contact between reagents and catalyst, while in

Introduction

Alkyne hydration is an atom efficient^[1] reaction that converts triple bonds into carbonyl species. Nucleophilic attack of water to terminal alkynes can occur *via* a Markovnikov or anti-Markovnikov mechanism leading to ketones or aldehydes, respectively (Scheme 1). While the latter products are selectively formed with Ru(II) complexes as catalysts either in water-organic solvent mixtures^[2] or, as shown recently, in pure water using intrinsically water-soluble ligands,^[3] ketones are the preferred products when



Scheme 1. Addition of water to terminal alkynes can occur through the Markovnikov mechanism providing methyl ketones or the anti-Markovnikov mechanism with formation of the corresponding aldehydes.

organic-water media in the absence of surfactants the reaction is sluggish. Hydration products can be isolated by means of extraction with an apolar solvent and the catalyst, that remains confined in the aqueous phase, can be recycled up to four times without loss of catalytic activity.

Keywords: alkynes; diphosphinamine ligands; micellar catalysis; platinum; water

Au^{I[4]} or Pt(II) species are employed. As far as the latter transition metal is concerned, early examples date back to the 1990s using chloro-platinum complexes without phosphine ligands, such as the Zeise's dimer^[5] or PtCl₄ in the presence of CO,^[6] both systems working in organic media such as wet THF. More recently intrinsically water-soluble monomeric dichloro Pt(II) complexes bearing sulfonated diphosphines have demonstrated good catalytic activity under mild experimental conditions but only with water-soluble alkynes bearing terminal hydroxy groups.^[7,8] Both with Ru(II)^[2a] and Pt(II)^[8] catalyzed alkyne hydration reactions, a strong influence by the ligand has been observed; in particular, bidentate diphosphine ligands with small bite angles provide much better catalytic performance compared to those with large bite angles either in pure water or in the presence of an organic co-solvent.

Since water is one of the reagents in the hydration reaction, its use as the solvent would be very convenient. Moreover, the replacement of organic and espe-

Adv. Synth. Catal. 2012, 354, 1095-1104

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cially chlorinated solvents with more environmentally friendly alternatives is one of the twelve principles of green chemistry.^[9] Solvents account for about 85%^[10] of the mass of chemicals in industrial productions and their recovery is usually only 80% efficient.^[11] Under this viewpoint, water represents the best solvent as it is extremely economic, non-toxic, non-flammable and its E factor is equal to zero.^[12] Even though it can be expensive to return water to a level of purity suitable for release in the environment,^[13] its use benefits also for the ease of catalyst recycling by means of biphasic extraction.

Unfortunately, solubility issues related to catalysts and substrates often make the employment of watermiscible co-solvents like acetone, dioxane, DMF and DMSO unavoidable. Using water-soluble ligands^[14] can overcome the problem only partially, as watersoluble substrates are often required that are difficult to isolate from the solution at the end of the reaction. The synthesis of such water-soluble ligands is also often far from straightforward. An alternative approach, avoiding the use of organic co-solvents but at the same time ensuring sufficient solubility to all species in water is based on the employment of surfactants added to the aqueous medium. Surfactants are amphiphilic species that self-assemble in water via hydrophobic effect leading to the formation of micelles of different nature. Micelles can act as nanometric apolar pools in water where both catalysts and substrates can be dissolved; higher local concentrations are experienced, often favouring catalytic activity and selectivity of organometallic reactions.^[15] Aqueous micellar media enable the use in water of a variety of complexes originally developed for work in organic solvents without the need to functionalize the corresponding ligands with hydrophilic groups to make the entire complex water-soluble, thus allowing a facile catalyst tuning without extra synthetic elaboration. This approach has been successfully applied to oxidation,^[16] hydrogenation,^[17] C–C bond formation^[18] and hydroformylation reactions^[19] resulting in most cases in enhancement of catalytic activity and selectivity compared to the same catalytic system running in organic media.

The present contribution deals with the development of new bis-cationic Pt(II) complexes bearing small bite angle diphosphinamine or N,N-bis(diarylphosphino)amine 'PNP' ligands^[20] for the efficient alkyne hydration reaction in water in the presence of surfactants under micellar conditions. In particular, the micellar medium facilitates the reaction and enables the recycling of the catalytic system (Scheme 2).



Scheme 2. Diphosphinamine ligands 1a–d, diphosphinediamine 1e and diphosphine ligands 1f, g used for the synthesis of bis-cationic Pt(II) complexes 3a–g.

Results and Discussion

Synthesis of Pt(II) Diphosphinamine cCmplexes 3a-e

PNP ligands have been recently developed for ethylene trimerization with Cr catalysts.^[21] These ligands are remarkably stable (air, water, acid, temperature resistant) and their synthesis is very straightforward. They may be predicted to have similar properties to bis(diarylphosphino)-methane or -ethane derivatives; however, surprisingly, they give much improved catalytic performance with respect to these more traditional ligands.^[20,21] With the aim of developing new robust Pt(II) hydration catalysts able to resist several reaction cycles in different media, we decided to choose some PNP ligands bearing different groups on the nitrogen and phosphorus atoms for the synthesis of a series of bis-cationic complexes of general formula [Pt(PN(N)P)(OH₂)₂](OTf)₂.

All the PN(N)P complexes were prepared according to the general routes shown in Scheme 2, starting from $[PtCl_2(COD)]$ by treatment with one equivalent of the corresponding diphosphinamine leading to the corresponding dichloro Pt(II) species [PtCl₂(PNP)] 2a-e isolated as white powders in good yields (higher than 95%). The bis-triflate complexes **3a-e** were prepared from the dichloro complexes **2a–e** by treatment with 2 equivalents of silver triflate in a wet solvent and obtained as air-stable white powders in medium to good yields (up to 97%). All the synthesized complexes were characterized by elemental analysis and multinuclear NMR spectroscopy. The ³¹P NMR Pt-P coupling constants for the bis-triflate complexes 3ae are in the order of 3700 Hz and generally higher than that observed for the bis-triflate complex bearing bis(diphosphino)methane $({}^{1}J_{Pt,P}=3316 \text{ Hz}),{}^{[22]}$ indicating a higher rigidity compared to this PCP backbone. This is consistent with the observation that the formal nitrogen lone pair is actually delocalized over the entire PNP backbone.^[20]

Worthy of note is the marked increase of the ${}^{1}J_{Pt,P}$ in the case of complex **3e** indicating an increased steric hindrance of the diphosphinodiamine **1e** (with the N–N bridge) compared to the less bulkier PNP ligands **1a–d**. In the series **3a–d**, the high value of the ${}^{1}J_{Pt,P}$ observed for complex **3d** can be associated also with a very weak Pt–O bond *trans* to the P atom, possibly due to the intramolecular coordination of the methoxy oxygen of the ligand. Two more bis-cationic complexes **3f** and **3g** bearing diphosphine ligands **1f** and **1g**, whose synthesis and characterization are reported in the literature,^[22,23] have been included in the study in order to compare their catalytic activity with those of PNP complexes **3a–e**.

Solubilization of the Pt(II) Complexes in the Micellar Media

None of the complexes bearing diphosphinamine ligands prepared in the present work is intrinsically soluble in water as tested by recording ¹H, as well as ³¹P NMR spectra in D_2O .

Conversely, in the presence of SDS (sodium dodecyl sulfate) as surfactant above its critical micellar concentration (c.m.c.), all complexes became soluble in D₂O and good ¹H, ³¹P and 2D NOESY and DOSY NMR experiments could be recorded. In Figure 1 are reported the spectra for complex **3d**. Apart from the resonances of the surfactant, the ¹H NMR spectrum clearly shows the aromatic resonances of the complex at 7.73 (t), 7.53 (dd) and 7.13 (m) ppm and the signals of the ligand at 3.52 (s) ppm for the methoxy moieties and at 2.65 (t) ppm for the N–CH₃ residue. The ³¹P NMR spectrum shows a singlet at 10.63 ppm with ${}^{1}J_{P,Pt}$ coupling constant of about 3765 Hz typical for bis-triflate complexes and similar to what is observed in CD₂Cl₂ (${}^{1}J_{Pt,P}$ =3767 Hz, see Experimental Section). Interaction of the bis-cationic Pt(II) species with the micelles is provided observing the DOSY spectrum that shows similar diffusion coefficients for the aromatic residues of the complex and the resonances of the surfactant. A NOESY experiment did not show cross peaks between the Pt(II) complex and the surfactant which means that it is likely that the bis-cationic complex is dissolved in water *via* formation of ion pairing with the anionic surface of the micelles without being directly in contact with the alkyl chains of the surfactant.

Catalytic Tests

The hydration reaction of 1-octyne as a model substrate has been used as a test reaction to screen different Pt(II) complexes (Table 1). Intrinsically watersoluble catalyst 3g^[24] bearing a small bite angle diphosphine showed modest catalytic activity at room temperature as well as at 50°C probably because of the difficult interaction between the apolar substrate dissolved within the micelles and the catalyst that resides in water. By contrast, catalyst **3f** is soluble only under micellar conditions^[19] and this would allow its intimate contact with the alkyne in the micelles. Nevertheless, the large bite angle disfavours the reaction and the product yield did not exceed 18%. We then tested diphosphinamine-based Pt(II) catalysts bearing aryl residues under micellar conditions initially using SDS as surfactant. Complex 3e bearing PNNP ligand **1e** and forming a five-membered ring Pt(II) complex showed lower catalytic activity compared to PNP analogues. Among the latter, a large difference in catalytic activity was observed depending on the substituents of the aryl residues of the ligands. Catalyst 3a showed good catalytic activity leading to 2-octanone in 63% yield, which increased up to 77% with catalyst 3b where the benzyl residue on the nitrogen atom probably favours a different, more active conformation of the catalyst compared to 3a. The presence of ethyl substituents on the aryl groups on one of the P donors, like in catalyst **3c**, causes a drastic drop in catalytic activity, while the presence of o-methoxy substituents increased the efficiency leading to 87% yield. The best catalyst proved to be **3d** both working at room temperature and at 50°C, confirming that for this kind of reaction small bite angle ligands are better than large ones in agreement with previous studies.^[2a,8] It is worth noting that the same ligand showed the best catalytic performance also for the Crcatalyzed trimerization of ethylene at low pressures, underlying the importance of o-OMe residues in the aromatic rings of diphosphinamine ligands that (as



Figure 1. ¹H, ³¹P, 2D-DOSY and NOESY spectra of the complex 3d (4 mM) in D₂O in the presence of SDS (80 mM).

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Table 1. Screening of Pt(II) catalysts **3a–g** in the hydration reaction of 1-octyne in water with SDS as surfactant.^[a]

$$R^{1} \xrightarrow{\text{Sa-g (2 mol\%)}} R^{1}$$

 $R^1 = C_5 H_{11}$

#	Catalyst	Cat. loading [mol%]	Temp. [°C]	Yield [%])
1	3g	0.5	25	6
	0	2		15
2		2	50	39
3	3f	2	25	7
4			50	18
5	3a	2	25	16
			50	63
6	3b	2	50	77
7	3c	2	25	11
			50	20
8	3d	2	25	39
			50	87
9	3e	2	25	4
			50	14

[a] Experimental conditions: [1-octyne]=0.2 M; water 0.5 mL; [surfactant]=0.08 M; 20 h. Yield determined by GC analysis.

well as any electronic or steric effect on catalysis) provide an extra weakly coordinating group that can be displaced by the incoming substrate.

We then investigated different reaction media such as biphasic chloroform-water, or single phase water with organic co-solvents and a wide range of surfactants. All systems including water-soluble or water-insoluble organic solvents were unsatisfactory leading to very low conversions (Table 2, entries 1-3). Water with a neutral surfactant like Triton X-100 did not improve the yield (Table 2, entry 9), probably because of poor catalyst solubilization. A cationic surfactant like CTABr could not be used since the anionic halogen atom coordinates to the catalyst leading to the inactive dibromo species. Charged zwitterionic surfactant (Table 2, entry 8) and anionic surfactants allowed good catalytic activity (Table 2, entries 4-7), in particular SDS showed the best performance with yield up to 87%. The amount of surfactant was optimized as reported in Table 3, observing that at 70°C the yield in ketone increases up to a 92% for 80 mM of SDS, followed by a decrease of activity for higher concentrations probably because of a dilution effect of the substrate in the micelles.

The much higher catalytic activity observed in the micellar medium compared to one- or two-phase water-organic media is probably due to the closer contact between catalyst and substrate when confined in the micelles compared to a bulk solvent. Micellar aggregates have been demonstrated to enhance the

Table 2.	Surfactant	screening	for the	hydration	reaction	of 1-
octyne v	with catalys	st 3d in wa	ter. ^[a]			

#	Cat. loading [mol%]	Medium	Temp. [°C]	Yield [%]
1	2	H ₂ O/CHCl ₃	50	6 ^[b]
2	2	H ₂ O-acetone	50	4
3	2	H ₂ O-dioxane	50	3
4	2	H ₂ O/SDS	50	87
5	1	H ₂ O/SDS	70	64
6	1	H ₂ O/SDSU	70	41
7	2	H ₂ O/SDBS	50	54
8	2	H ₂ O/zwitterion- ic	50	73
9	2	H ₂ O/Triton X- 100	50	8

 [a] Experimental conditions: [1-octyne]=0.2M; [3d]= 2 mol%, water 0.5 mL; [surfactant]=0.08M; 20 h. Yield determined by GC analysis.

^[b] Formation of oligomers has been observed.

Table 3. Effect of different SDS loadings in the hydration of 1-octyne with catalyst 3d in water.^[a]

ℝ ¹	3d (1 mol%)	U _R1
Ŷ	H ₂ O/SDS, 70 °C	~ ~

 $R^1 = C_5 H_{11}$

#	Surfactant [mM]	Yield [%]
1	40	71
2	80	92
3	120	48
4	240	52

 [a] Experimental conditions: [1-octyne]=0.4 M; [3d]= 1 mol%, water 0.5 mL; T=70 °C, 20 h. Yield determined by GC analysis.

catalytic activity compared to *i*-PrOH-water medium in alkyne hydration reactions even when mediated by Ru(II) catalysts.^[25] Recently, other Pt(II)-catalyzed reactions on water-soluble alkynes have been shown to benefit greatly from the use of water as the sole solvent compared to organic media, underlying the positive role played by aqua-Pt(II) species.^[26]

With the best catalytic system based on complex **3d** and 80 mM SDS as surfactant we investigated the scope of the reaction on a series of different terminal as well as internal alkynes. Aromatic terminal alkynes are converted to the corresponding substituted acetophenones in quantitative yields (Table 4, entries 1–3). Solid aromatic alkynes (entries 4 and 5) showed reduced activity because of much more difficult substrate solubilization in the micellar media, and aromatic electron-poor alkynes bearing competitive ligands for the metal center like 4-ethynylpyridine did

	R^1	$\begin{array}{ccc} \mathbf{3d} & 0 \\ \mathbf{3d} & (2 \mod 8) \\ \mathbf{z} & \mathbf{R}^1 & \mathbf{R}^2 \end{array}$	
	Ý	H ₂ O/SDS, 80 °C	
#	Substrate	Product	Yield [%] ^[b]
1		o	>98 (89)
2			>98
3			97
4 ^[c]			26
5 ^[c]			32
6			97 (85)
7			>98 (82)
8	X-	o V	83
9	ОН	ОН	11
10		O L	>98
11			>98 (68:32) ^[d]
12	ОН	ОЦОН	71

Table 4. Substrate scope of the hydration reaction with catalyst 3d in water with SDS as surfactant.^[a]

^[a] Experimental conditions: [alkyne]=0.2 M; [3d]=2 mol%, water 0.5 mL; [surfactant]=0.08 M; T=80 °C, 20 h. Yield determined by GC analysis and product assignment via ¹H NMR.

^[b] Isolated yield in brackets.

^[c] Solid alkyne substrate.

^[d] Ratio between regioisomers.

not react at all. Alkyl-substituted terminal alkynes turned out to be good substrates leading to quantitative formation of the corresponding methyl ketone (entries 6 and 7). The hindered en-yne substrate bearing a camphor-like scaffold (entry 8) reacted as expected leading to the corresponding methyl ketone in good yield (83%). If the substrate is intrinsically water-soluble like in the case of 3-butyn-1-ol (entry 9) it does not interact well with the micelles and this turned out in lower yields in the corresponding ketone. The symmetrical internal alkyne 3-hexyne was converted into the corresponding 3-hexanone in 98% yield (entry 10), while for unsymmetrical internal alkynes (entries 11 and 12) the selectivity was dependent on the presence of intramolecular nucleophiles while activity is related to the affinity of the Table 5. Recycle tests for the hydration of phenylacetylene with catalyst 3d in water.^[a]



^[a] Experimental conditions: [phenylacetylene]=0.2 M; [3d]=4 mol%, [SDS]=0.08 M; water 1.5 mL, T=80 °C, 20 h. Yield determined by GC analysis.

substrate for the micelles where the catalyst is positioned. In fact apolar 3-phenylpropyne was quantitatively converted into the corresponding ketones with a 68: 32 ratio between addition to C-3 compared to C-2, in agreement with the Markovnikov rule and with selectivity similar to what is observed with other Pt(II)-based systems (entry 7).^[6] Conversely, for the intrinsically water-soluble 3-pentyn-1-ol a maximum vield of 71% was obtained because of its lower affinity for the micellar aggregates (entry 8) and the only observed product was 5-hydroxy-2-pentanone that forms by activation of the triple bond by Pt(II) followed by intramolecular addition of the terminal alcohol to the C-4 of the alkyne residue forming a fivemembered ring cyclic intermediate that is quickly disrupted by water addition to the final ketone.^[7,8]

The use of a micellar phase containing the active Pt(II) complex provides a direct access to catalyst recycling by simple extraction of the organic product with a highly apolar solvent like hexane and reuse of the aqueous solution where the catalyst remains confined being completely insoluble in alkanes. It is worth noting that the bis-cationic monomeric catalysts bearing diphosphinamine ligands are obtained by precipitation with pentane from a chloroform solution.

The recycling experiments were carried out at 80°C, with 4 mol% 3d catalyst loading with respect to phenylacetylene selected as a model substrate and a double concentration of SDS as surfactant to ensure solubilization of both **3d** and the substrate. The results of the recycling experiments are reported in Table 5. Even though a certain degree of catalyst deactivation occurs, as observed considering the TOF of the catalyst, quantitative formation of the hydration product can still be obtained after 20 h at 80 °C for a total of three recycles. The ion pairing between the bis-cationic catalyst and the anionic nature of the micelles is the driving force to ensure stabilization and confinement of the catalyst in the aqueous phase during extraction of the apolar organic products with hexane as organic phase.

Mechanistic Investigation

In order to shed light into the different behaviour of catalyst **3d** in organic media such as chloroform, acetone and dioxane compared to aqueous micellar media as reported in Table 2, we performed a series



Figure 2. A) ³¹P NMR of the species present in solution arising from complex **3d** (2 mM) in CDCl₃ in the presence of phenylacetylene (50 mM); **B**) ³¹P NMR of the species present in solution arising from complex **3d** (2 mM) in H₂O-SDS (80 mM) in the presence of phenylacetylene (50 mM).

Adv. Synth. Catal. 2012, 354, 1095-1104

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of NMR experiments showing the formation of different Pt(II) species present in organic solvent with respect to the aqueous phase. In particular, catalyst **3d** (2 mM) in chloroform-*d* in the presence of fifty equivalents of phenylacetylene led, after a few minutes, to the formation of a new symmetrical species characterized by an up-field shifted ³¹P NMR signal at 9.8 ppm with an unusually large $J_{P,Pt}$ of 4146.6 Hz (Figure 2). By contrast, catalyst **3d** (2 mM) in D₂O with SDS (80 mM) with an excess of phenylacetylene provided a completely different species characterized by a ³¹P NMR resonance at 22.7 ppm with a much smaller J_{PPt} of 2263.2 Hz (Figure 2).

While the former species is likely to be a bidentate diphosphine Pt(II) complex with two neutral π coordinated species that give rise to such high value for the $J_{P,Pt}$ coupling constant,^[27] in anionic micellar media the smaller $J_{P,Pt}$ coupling constant is in agreement with σ coordination on Pt(II). Attempts to isolate such intermediate species failed and a careful ¹H NMR analysis revealed the presence of a weak triplet at 3.67 ppm with ³ $J_{H,P}$ of 7.76 Hz which is attributable to a C_2 -symmetrical Pt–CH₂–COPh residue^[28,29] that are known to be intermediate species^[7,8] in the hydration catalytic cycle mediated by Pt(II) catalysts and that recently have been fully characterized by Hahn.^[29]

It is worth noting that alkynes are sufficiently electron rich to provide coordination to **3d** displacing the weakly coordinating triflate anion as observed in H_2O -CDCl₃ solution, but only in H_2O -SDS micellar medium do such species undergo Markovnikov addition of water to the triple bond leading to neutral disubstituted σ Pt-vinyl species. Moreover the Brønsted acidity provided on the surface of the anionic micelles favours the hydrogenolysis of σ Pt-vinyl residues leading to turnover of the system and release of the methyl ketone hydration product.

Conclusions

In the present contribution we have developed new monomeric bis-cationic Pt complexes bearing small bite angle diphosphinamine PNP ligands for highly active alkyne hydration reactions operating in aqueous micellar conditions and selectively leading to the corresponding Markovnikov carbonyl compounds. Interaction with the micelles enables catalyst solubilization in water of both catalyst and substrates and, at the same time, enhances greatly the catalytic activity compared to the reaction performed in homogeneous binary solvent mixtures like acetone-water, dioxanewater or biphasic CHCl₃/water 1:1. The specific role played by the micellar aqueous medium is to favour the formation of catalytically active Pt(II) species bearing σ vinyl residues while in organic media with

water the reaction stops at forming the π coordinated alkyne species. The strong interaction between the bis-cationic catalyst and the anionic micelles allows the reuse for four cycles without significant loss of catalytic activity. The Pt(II) catalytic system remains confined in the aqueous phase while the product was isolated by extraction with hexane.

Experimental Section

Reagents and Materials

General: ¹H NMR, ³¹P{¹H} NMR, and ¹⁹F NMR spectra were run on a Bruker AC200 spectrometer operating at 200.13, 81.015, and 188.25 MHz, respectively, at 298 K, unless otherwise stated; δ values in ppm are relative to Si(CH₃)₄, 85% H₃PO₄, and CFCl₃. All reactions were monitored by GC analysis, measurements were taken on a Hewlett–Packard 6890A gas chromatograph equipped with a FID detector (carrier gas He).

Substrates: All the alkynes used as substrates are commercial products (Aldrich) and were used without any purification. All the surfactants and water-soluble additives are commercial products and were used without purification: SDS sodium dodecyl sulfate, zwitterionic *N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate, Triton X-100 polyoxyethylene(10)isooctyl phenyl ether, SDSU sodium dodecyl sulfonate.

Synthesis of the Complexes

All the synthetic work was carried out with the exclusion of atmospheric oxygen under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified according to standard methods. AgOTf (Aldrich) was a commercial product and used without purification. The ligands $1c^{[21b]}$ and $1d^{[20]}$ and the complexes $[PtCl_2(1a)]$ (2a),^[30] $[PtCl_2(1b)]$ (2b),^[31] $[PtCl_2(1e)]$ (2e),^[32] $[Pt(OH_2)_2(1f)]$ (OTf)₂ (3f)^[23] and $[Pt(OH_2)_2(1g)]$ (OTf)₂ (3g)^[22] were synthesized following the procedures reported in the literature.

Synthesis of [PtCl₂(1c)] (2c): To a solution of the complex [PtCl₂(COD)] (66.1 mg, 0.177 mmol) in 30 mL of dichloromethane at room temperature was added **1c** (90.3 mg, 0.198 mmol). The solution was stirred under nitrogen overnight observing the formation of a white precipitate. After concentration, the white precipitate was filtered off, washed with *n*-hexane and dried under vacuum; yield: 122.1 mg (95.8%). Anal. calcd. for C₂₉H₃₁Cl₂NP₂Pt: C 48.28, H 4.33, N 1.94%; found: C 48.12, H 4.32, N 1.92%; ¹H NMR (CD₂Cl₂): δ =1.05 (br, ArCH₂CH₃), 2.68 (t, ³J_{PH}=12 Hz, NCH₃), 2.85 (br, ArCH₂CH₃), 7.82–7.29 (m, Ar); ³¹P[¹H] NMR (CD₂Cl₂): δ =13.46 (d, ¹J_{PtP}=3362 Hz, ²J_{PP}= 38 Hz), 15.50 (d, ¹J_{PtP}=3229 Hz, ²J_{PP}=38 Hz).

Synthesis of [PtCl₂(1d)] (2d): To a solution of the complex [PtCl₂(COD)] (79.6 mg, 0.213 mmol) in 30 mL of dichloromethane at room temperature was added 1d (111.6 mg, 0.214 mmol). After few minutes a white precipitate starts forming. The reaction mixture was stirred under nitrogen overnight. After concentration, the suspension was treated with *n*-hexane and the white precipitate was filtered off, washed with *n*-hexane and dried under vacuum; yield: 159.3 mg (95.3%). Anal. calcd. for $C_{29}H_{31}Cl_2NO_4P_2Pt$: C 44.34, H 3.98, N 1.78%; found: C 44.31, H 3.35, N 1.77%; ¹H NMR (CD₂Cl₂): δ =2.75 (t, ³*J*_{P,H}=12 Hz, NCH₃), 3.40 (s, OCH₃), 8.00–6.92 (m, Ar); ³¹P{¹H} NMR (CD₂Cl₂): δ =10.03 (s, ¹*J*_{P,L}=3352 Hz).

Synthesis of [Pt(OH₂)₂(1a)](OTf)₂ (3a): To a solution of [PtCl₂(1a)] (0.15 g, 0.22 mmol) in 30 mL of wet dichloromethane at room temperature was added 3.2 mL (0.45 mmol) of a 1.4M acetone solution of AgOTf. The reaction mixture was stirred under nitrogen for 2 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with *n*-pentane. The white precipitate was filtered off, washed with *n*-pentane and dried under vacuum; 194.2 mg (97.5%). yield: Anal. calcd. for C₂₉H₃₁F₆NO₈P₂PtS₂: C 36.41, H 3.27, N 1.46%; found: C 36.29, H 3.27, N 1.46%; ¹H NMR (CD₂Cl₂): $\delta = 0.75$ (d, CH₃, ${}^{3}J_{H,H} = 8$ Hz), 3.56 (sp, CH, ${}^{3}J_{H,H} = 8$ Hz), 8.08–7.64 (m, Ar); ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂): $\delta = 1.63$ (s, ${}^{1}J_{Pt,P} = 3755$ Hz); ¹⁹F NMR (CD₂Cl₂): $\delta = -81.44$ (s, OTf).

Synthesis of [Pt(OH₂)₂(1b)](OTf)₂ (3b): The compound **3b** was prepared according to a similar procedure as for the complex **3a** starting from [PtCl₂(**1b**)] (150.0 mg, 0.20 mmol) and 2.9 mL (0.41 mmol) of a 1.4M acetone solution of AgOTf; yield: 145.7 mg (74.7%). Anal. calcd. for $C_{34}H_{33}F_6NO_8P_2PtS_2$: C 40.08, H 3.26, N 1.37%; found: C 39.96, H 3.27, N 1.37%; ¹H NMR (CD₂Cl₂): $\delta = 1.11$ (d, CH₃, ³J_{H,H} = 6 Hz), 4.52 (m, CH), 6.69 (d, *o*-Ar), 7.00 (t, *m*-Ar), 7.17 (t, *p*-Ar), 7.87–7.60 (m, PAr); ³¹P{¹H} NMR (CD₂Cl₂): $\delta = -81.87$ (s, OTf).

Synthesis of [Pt(OH₂)₂(1c)](OTf)₂ (3c): The compound 3c was prepared according to a similar procedure as for the complex 3a starting from [PtCl₂(1c)] (101.2 mg, 0.14 mmol) and 2.0 mL (0.28 mmol) of a 0.14 M acetone solution of AgOTf; yield: 104.5 mg (78.2%). Anal. calcd. for $C_{31}H_{35}F_6NO_8P_2PtS_2$: C 37.81, H 3.58, N 1.42%; found: C 37.64, H 3.59, N, 1.42%; ¹H NMR (CD₂Cl₂): δ =1.03 (br, ArCH₂CH₃), 2.65 (t, ³J_{PH}=12 Hz, NCH₃), 2.85 (br, ArCH₂CH₃), 7.84–7.36 (m, Ar); ³¹P{¹H} NMR (CD₂Cl₂): δ = 3.59 (d, ¹J_{Pt,P}=3701 Hz, ²J_{P,P}=42 Hz), -2.72 (d, ¹J_{Pt,P}=3707 Hz, ²J_{P,P}=42 Hz); ¹⁹F NMR (CD₂Cl₂): δ =-81.73 (s, OTf).

Synthesis of [Pt(OH₂)₂(1d)](OTf)₂ (3d): To a suspension of [PtCl₂(1d)] (140.6 mg, 0.179 mmol) in 30 mL of acetone at room temperature was added AgOTf (93.0 mg, 0.362 mmol). The reaction mixture was stirred under nitrogen for 2 h and then taken to dryness. The resulting solid was treated with 30 mL of dichloromethane and the solid AgCl filtered off. After concentration, the solution was treated with *n*-hexane. The white precipitate was filtered off and dried under vacuum; yield: 138.8 mg (76.6%). Anal. calcd. for $C_{31}H_{35}F_6NO_{12}P_2PtS_2$: C 35.50, H 3.36, N 1.34%; found: C 35.41, H 3.37, N 1.33%; ¹H NMR (CD₂Cl₂): δ = 2.87 (t, ³J_{P,H}=12 Hz, NCH₃), 3.54 (s, OCH₃), 7.75–6.99 (m, Ar); ³¹P{¹H} NMR (CD₂Cl₂): δ = -81.97 (s, OTf).

Synthesis of $[Pt(OH_2)_2(1e)](OTf)_2$ (3e): The compound 3e was prepared according to a similar procedure as for the complex 3d starting from $[PtCl_2(1e)]$ (65.8 mg, 0.09 mmol) and AgOTf (46.5 mg, 0.18 mmol); yield: 69.8 mg (81.4%). Anal. calcd. for $C_{32}H_{38}F_6N_2O_8P_2PtS_2$: C 37.91, H 3.78, N 2.76%, found: C 37.79, H 3.78, N 2.75%; ¹H NMR (CDCl₃):

δ=2.53 (br, ArCH₃), 2.77 (br, NCH₃), 7.61–7.35 (m, Ar); ³¹P{¹H} NMR (δ, CDCl₃): δ=87.46 (s, ¹*J*_{Pt,P}=4762 Hz); ¹⁹F NMR (CDCl₃): δ=-82.08 (s, OTf).

Catalytic Studies: General Procedure for the Catalytic Reactions

The proper amount of surfactant (80 mM) was placed in a 3-mL vial equipped with a screw capped septum and to this water (0.5 mL) and Pt(II) catalyst **3a–g** (2 mol%) were added. The system was stirred vigorously for 5 min, followed by addition of the alkyne (0.2 M) and the vial was thermostatted at the desired temperature under stirring for the indicated time. Subsequently the sample was cooled to room temperature, the mixture extracted with an equal volume of ethyl acetate and the organic phase separated, treated with Na₂SO₄ and analyzed *via* GC on a column HP-5, He 1 mLmin⁻¹, 150 °C for 5 min and 2 °Cmin⁻¹ to 200 °C. Quenching of the reaction was not necessary.

General Procedure for Recycle Experiments

The proper amount of surfactant (SDS 160 mM) was placed in a 10-mL vial equipped with a screw capped septum and to this water (5 mL) and Pt(II) catalyst 3d (4 mol%) were added. The system was stirred vigorously for 5 min, followed by addition of the alkyne substrate (0.2 M) and the vial was thermostatted at the desired temperature under stirring for the indicated time. Subsequently the sample was cooled to room temperature, the mixture extracted with an equal volume of hexane, the organic phase separated, treated with Na₂SO₄ and analyzed via GC on a column HP-5, He 1 mLmin⁻¹, 150 °C for 5 min and 2 °Cmin⁻¹ to 200 °C. The aqueous phase containing the surfactant and the catalyst were placed back in a 10-mL vial equipped with a screw capped septum, to this alkyne substrate (0.2 M) was added and the vial was thermostatted at the desired temperature under stirring for the indicated time for the recycle experiment.

Acknowledgements

The authors thank the British Research Council and the Italian CRUI for funding the "British-Italian Partnership Programme for Early Careers Researchers 2009–2010". MIUR, Universitá Ca' Foscari di Venezia, Università degli Studi di Padova and "Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali" are acknowledged for financial support. G.S. thanks Johnson-Matthey for the loan of platinum. The University of Bristol is thanked for the award of a university scholarship (to A.M.C.). The help of L. Sperni for GC-MS analysis is gratefully acknowledged.

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