Minor Modifications to the Ligands Surrounding a Ruthenium Complex Lead to Major Differences in the Way in which they Catalyse the Hydrogenation of Arenes

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Abstract: The hydrogenation of benzene and other arenes under aqueous-organic biphasic conditions is evaluated using the ruthenium complexes Ru(η^6-$C_{10}H_{14}$)(pta)Cl_2 (pta = 1,3,5-triaza-7-phosphaadamantane), Ru(η^6-$C_{10}H_{14}$)(tppts)Cl_2 (tppts = tris-3-sulfonatophenylphosphine trisodium salt) and [Ru(η^6-$C_{10}H_{14}$)(pta)$_2$Cl]$^+$. The active catalysts formed during the hydrogenations correspond to a trinuclear cluster, a colloid and a mononuclear complex, respectively.

Keywords: arenes; biphasic catalysis; cluster catalysis; hydrogenation; P-ligands; ruthenium

Introduction

The reduction of arenes is an important reaction in organic synthesis, the preparation of cleaner fuels and in paper production.[1] While stoichiometric reagents are often used arene hydrogenation catalysts are becoming increasingly employed and they are dominated by the platinum group metals, especially the elements ruthenium and rhodium. The majority of catalysts are heterogeneous, and although a number of molecular compounds have been reported to homogeneously catalyse the hydrogenation of arenes, many have since been found to undergo transformations to colloids during reaction. As such, the whole concept of homogeneous arene hydrogenation catalysis has been called into question.[2]

It would appear that the majority of rhodium catalysts, including [Rh(η^5-C_5Me_5)Cl_2]$_2$,[3] [Rh(η^4-C_6H_8-1,4)Cl]$_2$,[4] Rh(η^4-C_8H_{10}-1,5)(Ph_2PCH_2COO) and Rh(CO)$_2$(Ph_2PCH_2COO)[5] form colloids which catalyse the hydrogenation of arenes. These compounds are either not active for the hydrogenation of polymer-bound benzene derivatives,[6] or turnovers vary with time;[7] both phenomena are indicative of colloidal catalysis. As a prominent example, [$RhCl_4$]$^-$ was initially believed to be a homogeneous arene hydrogenation catalyst, but later catalytic activity was shown to be based on rhodium nanoclusters.[8]

The possibility that ruthenium complexes act as homogeneous arene hydrogenation catalysts seems more promising. The complexes Ru(η^6-C_6Me_6)(PPh_3)(H)Cl and [(η^6-C_6Me_6)Ru(μ-H)$_2$(μ-Cl)Ru(η^6-C_6Me_6)]$^+$ are effective catalysts, but catalyst decomposition is observed and this is often indicative of colloid formation.[9] The bis-hexamethylbenzene complex, Ru(η^6-C_6Me_6)(η^4-C_6Me_6) is also an active catalyst for arene hydrogenation, but whether or not the catalyst is homogeneous remains a matter of some doubt.[10] The stereoselectivity was not particularly high for the hydrogenation of xylenes and cyclohexenes were obtained in some quantity from the hydrogenation of benzene. One of the most recent homogeneous arene hydrogenation catalysts based on ruthenium is $RuH_2(H_2)_2(PCy_3)_2$, however, the addition of mercury to the reaction reduced the activity to zero, thereby suggesting that the active catalyst is colloidal.[11] The complex [Ru(η^6-$C_{10}H_{14}$)(η^2-triphos)Cl]$^+$ has been shown to catalyse the hydrogenation of arenes in dichloromethane and ionic liquids.[12] It would appear to act in a homogeneous fashion although no decomposition or loss of activity is observed in the ionic liquid and some decomposition takes place in dichloromethane. In this paper we show that closely related water-soluble ruthenium complexes can catalyse the hydrogenation of arenes in very different ways.

Results and Discussion

The compounds Ru(η^6-$C_{10}H_{14}$)(pta)Cl_2 **1** (pta = 1,3,5-triaza-7-phosphaadamantane), Ru(η^6-$C_{10}H_{14}$)(tppts)Cl_2 **2** (tppts = tris-3-sulfonatophenylphosphine trisodium salt) and [Ru(η^6-$C_{10}H_{14}$)(pta)$_2$Cl]$^+$ **3** (Scheme 1) were prepared for evaluation as catalysts for the hydrogena-

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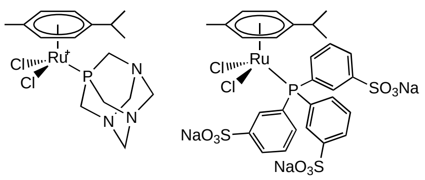

1 **2** **3**

Scheme 1.

tion of arenes under biphasic conditions. A number of ruthenium-pta[13] and -tppts[14] complexes have shown to catalyse the reduction of other substrates in water. Compound **1** is known,[15] whereas **2** and **3** have not been reported previously. Compound **2** was prepared in an analogous manner to **1**, *viz.* from the direct reaction of the dimer $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2]_2$ with two equivalents of tppts in methanol. The negative ion electrospray mass spectrum of **2** exhibits a single peak at *m/z* 851 which corresponds to the ion $[Ru(\eta^6\text{-}C_{10}H_{14})(tppts)Cl_2-Na]^-$ due the loss of a sodium ion from the tppts ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2** in D_2O shows a singlet resonance at 34.81 ppm which corresponds to co-ordinated tppts. The ^1H NMR spectrum of **2** in CD_3OD shows a broad multiplet at 8.30–7.60 ppm, which can be attributed to the tppts ligand phenyl rings. A further multiplet at 5.90–5.30 ppm corresponds to the aromatic ring protons of the *p*-cymene ring. The distinctive septet resonance at 2.55 ppm ($J = 7.32$ Hz) is readily assigned to the single CH proton of the isopropyl grouping of the *p*-cymene ligand. A doublet at 0.99 ppm ($J = 7.11$ Hz) can be assigned to the methyl group proton of the same group. One final singlet resonance at 1.77 ppm occurs due to the methyl group attached directly to aromatic ring.

Compound **3** is derived from **1** by reaction with one equivalent of pta together with one equivalent of silver tetrafluoroborate in dichloromethane. It is not too dissimilar from the tppts complexes $[Ru(\eta^6\text{-arene})(tppts)_2H]^+$ described previously, although prepared by a different route.[16] The positive ion electrospray mass spectrum of **3** contains a peak at *m/z* 585 which corresponds to the cation $[Ru(\eta^6\text{-}C_{10}H_{14})(pta)_2Cl]^+$ and a lower intensity peak at *m/z* 428 due to the presence of $[Ru(\eta^6\text{-}C_{10}H_{14})(pta)Cl]^+$ derived from the molecular ion by loss of a pta group. The $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ contains a singlet at -32.97 ppm, which corresponds to the co-ordinated pta ligands. Two sets of well-defined peaks corresponding to the *p*-cymene ring and the pta ligand are observed. A quartet at 5.45 ppm ($J = 6.42$ Hz) can be assigned to the aromatic ring protons of the co-ordinated *p*-cymene ring. The distinctive septet of the *p*-cymene ligand at 2.79 ppm ($J = 6.55$ Hz). The methyl group protons of the isopropyl group give rise to a doublet at 1.28 ppm ($J = 6.55$ Hz) and the singlet resonance at 2.08 ppm can be assigned to the remaining methyl group attached to the ring. The pta ligand gives rise to two further singlet resonances, a peak at 4.53 ppm may be assigned to the CH_2 protons in the nitrogen heterocycle and the peak at 4.32 ppm to the CH_2 protons in the phosphorus-nitrogen heterocycle.

Catalytic Evaluation of 1–3

Compounds **1–3** are highly water-soluble and were immobilised in water and tested for activity as pre-catalysts for the hydrogenation of arenes. The results from these studies are listed in Table 1. The two complexes with pta ligands, *viz.* **1** and **3**, exhibit similar turnover frequencies, although **1** is more active than **3**, whereas the tppts complex **2** is considerably more active than either of the pta complexes.

The reactions were repeated in the presence of mercury and with **1** and **3** no significant change in activity was observed. In contrast, the addition of mercury to the hydrogenations using **2** result in significantly reduced turnovers (see Table 2), which suggests that the activity is nearly entirely colloidal. ^{31}P NMR spectroscopy shows that the tppts dissociates, and since tppts can act as a surfactant,[17] it is not unreasonable to assume that it stabilises the colloids in aqueous solution. In other hydrogenations, e.g., CO_2 reduction in aqueous solution under similar conditions, there was no evidence for colloid formation using the same complex.[18]

Compounds **1** and **3** would appear to act as homogeneous catalysts for the hydrogenation of arenes. Examination of **1** after reaction by NMR spectroscopy and electrospray mass spectrometry shows that it undergoes a transformation to a triruthenium cluster that does not contain any pta. The ^1H NMR spectrum of the resulting complex shows that only the *p*-cymene ring remains attached. Loss of the phosphine is confirmed by $^{31}P\{^1H\}$ NMR spectroscopy, which shows that the phos-

Table 1. The hydrogenation of various arene substrates using **1–3** immobilised in water.[a]

Substrate	Catalyst	Turnover ($mol\ mol^{-1}\ h^{-1}$)
C_6H_6	**1**	170
C_6H_5Me	**1**	130
C_6H_5Et	**1**	122
C_6H_6	**2**	488
C_6H_5Me	**2**	365
C_6H_5Et	**2**	245
$C_6H_5{}^iPr$	**2**	98
C_6H_6	**3**	150
C_6H_5Me	**3**	129
C_6H_5Et	**3**	72

[a] Reaction conditions: catalyst (30 mg) in water (10 mL), substrate (1 mL), H_2 (60 atm) 90 °C, 1 h. Products formed were completely hydrogenated cyclohexane analogues of the respective substrate.

Table 2. The hydrogenation of various arene substrates using **2** immobilised in water with mercury added as a colloidal poison.[a]

Substrate	Turnover (mol mol^{-1} h^{-1})
C_6H_6	32
C_6H_5Me	4
C_6H_5Et	16
C_6H_5-*i*-Pr	2

[a] Catalyst (64 mg 0.0733 mmol), water (10 ml), arene substrate (1 mL), mercury (1 mL). Reaction time of 1 hour. Products formed were completely hydrogenated cyclohexane analogues of the respective substrate. Turnovers are quoted in number of moles of substrate converted per mole of catalyst per hour.

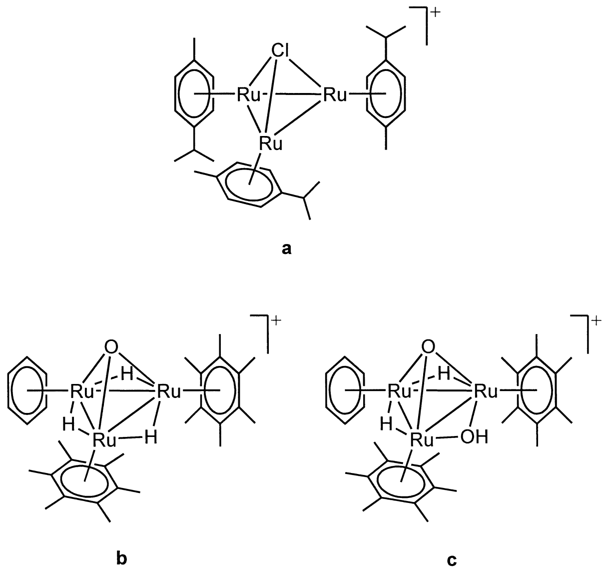

Figure 1. The proposed structure of the catalyst derived from **1**, *viz.* $[Ru_3(\eta^6\text{-}C_{10}H_{14})_3(\mu_3\text{-}Cl)]^+$; and the structures of (**b**) $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-}O)(\mu_2\text{-}H)_3]^+$ and (**c**) $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-}O)(\mu_2\text{-}H)_2(\mu_2\text{-}OH)]^+$.

phine ligand is no longer present. The positive ion electrospray mass spectrum exhibits a significant peak centred at *m/z* 743 which could correspond to a cluster of formula $[Ru_3(\eta^6\text{-}C_{10}H_{14})_3(\mu_3\text{-}Cl)]^+$ (in negative ion mode no peaks containing the ruthenium isotopomer are observed). Electrospray ionisation mass spectrometry has previously been shown to be very reliable for the characterisation of water-soluble organometallic clusters.[19] The valance electron count for a cluster of this formula is 46, two fewer than the number expected for a trinuclear (triangular) cluster. The electronic situation here, however, is not too dissimilar from that observed for the tetranuclear clusters $[H_4Ru_4(\eta^6\text{-arene})_4]^{2+}$, which are also active arene hydrogenation catalysts following addition of dihydrogen.[20] Unlike the tetraruthenium cluster, the *p*-cymene ligands present in the starting material do not exchange with the arene substrate. Such a situation is more typical of the clusters $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-}O)(\mu_2\text{-}H)_3]^+$, and $[Ru_3(\eta^6\text{-}C_6Me_6)_2(\eta^6\text{-}C_6H_6)(\mu_3\text{-}O)(\mu_2\text{-}H)_2(\mu_2\text{-}OH)]^+$.[21] In these clusters it has been proposed that the arene substrate interacts with the face of the triruthenium unit opposite to the μ_3-capping ligand, in a way not too dissimilar from the well characterised μ_3-η^2:η^2:η^2-arene co-ordinated mode,[22] but involving much weaker interactions. The proposed structure for the cluster generated from **1** is shown in Figure 1. We do not think that the cluster generated from **1** is the same as those mentioned above as the turnover numbers differ, and we do not observe hydrides on the material recovered after reaction. In an attempt to confirm the identity of the active arene hydrogenation catalyst generated from **1** an *in situ* NMR experiment was conducted. Compound **1**, benzene and water were pressured under 100 atmospheres of hydrogen in an NMR tube. The ^{1}H NMR spectrum immediately showed an intense doublet centred at -9.33 ($J = 57.6$ Hz). With time, this doublet decreases in intensity and a number of new hydride signals are observed between -10 and -20 ppm. While the identity of these hydride containing species remains unknown, they do not correlate to those of the trinuclear clusters reported by Süss-Fink.[20] However, it is well known that build-up of clusters in water from related ruthenium species can lead to a variety of different products depending upon the conditions.[23]

Conclusions

Homogeneous arene hydrogenation catalysts are few and far between and molecular ruthenium clusters probably represent the most thoroughly characterised examples. There has also been much discussion about the effectiveness of homogeneous cluster catalysis. Generally, clusters are not deemed to be as useful as mononuclear complexes in homogeneous catalytic applications. This is partly due to the complexity of the cluster reaction mechanism, for example, only very recently has direct evidence been presented which shows that catalysis by intact clusters takes place.[24] Whatever the problems associated with cluster catalysis, for arene hydrogenation reactions small metal clusters have proven to be very effective and they are superior to their mononuclear counterparts. It is even possible that many of the mononuclear complexes that have been shown to hydrogenate arenes actually do so after transforming into a cluster. While compound **3** described in this paper possibly represents an example of a mononuclear homogeneous arene hydrogenation catalyst further studies are required in order to confirm this hypothesis.

Experimental Section

The compounds 1,3,5-triaza-7-phosphaadamantane (pta)[25] and Ru(η^6-$C_{10}H_{14}$)(pta)Cl_2[15] were made according to the literature procedures. All other reagents were supplied by Aldrich and were used without further purification.

Electrospray mass spectra were obtained a VG Autospec instrument. NMR spectra were recorded on a Bruker DRX-400 spectrometer with ^{1}H at 400.13, ^{31}P at 161.98 and ^{13}C at 100.1 MHz. ^{1}H NMR chemical shifts are reported in ppm relative to residual ^{1}H signals in the deuterated solvents ($CDCl_3$ $\delta = 7.29$), $^{31}P\{^1H\}$ NMR spectra are reported in ppm downfield of an external 85% solution of phosphoric acid. All hydrogenation products were analysed by NMR and/or gas chromatography using a Varian gas chromatograph with a capillary carbowax column (30 m) using injection, oven and detector temperatures 10 – 30 °C above the boiling points of the substrate/product being studied.

Synthesis of Ru(η^6-$C_{10}H_{14}$)(tppts)Cl_2 (2)

A solution of [Ru(η^6-$C_{10}H_{14}$)Cl_2]$_2$ (153 mg, 0.25 mmol) and tppts (284 mg, 0.5 mmol) in methanol was heated to reflux for 5 h during which the solution changed from orange to deep red in colour. Removal of the solvent under reduced pressure followed by washing in dichloromethane (2 × 10 mL) and further drying on a vacuum line resulted in a dark red microcrystalline solid; yield: 400 mg (0.458 mmol, 92%). The product was used without further purification for the investigation of its catalytic properties.

Spectroscopic data for **2**: Negative ion ESMS: $m/z = 851$ [Ru(η^6-$C_{10}H_{14}$)(tppts)Cl_2 – Na]$^-$; $^{31}P\{^1H\}$ NMR (D_2O): $\delta = 34.81$ (s), 29.92 (s); ^{1}H NMR (CD_3OD): $\delta = 8.30 – 7.60$ (m, 12H), 5.90 – 5.30 (m, 4H), 2.55 (septet, $J = 7.32$ Hz, 1H), 1.77 (s, 3H), 0.99 (d, $J = 7.11$ Hz, 6H).

Synthesis of [Ru(η^6-$C_{10}H_{14}$)(pta)$_2$Cl][BF_4] (3)

pta (68 mg, 0.432 mmol, 1 equiv.) was added to a dichloromethane (25 mL) solution of Ru(η^6-$C_{10}H_{14}$)(pta)Cl_2 (200 mg, 0.432 mmol). On addition a slight colour change from deep red to red/orange takes place. Addition of silver tetrafluoroborate (84 mg, 0.432 mmol, 1 equiv.) in methanol solution (2 mL) gave an immediate colour change from red/orange to a yellow solution accompanied with the formation of a fine grey precipitate. The precipitate was removed *via* filtration on a glass microfibre filter apparatus. Removal of the solvent under reduced pressure followed by further drying on a vacuum line resulted in a yellow/orange solid; yield: 257 mg (0.382 mmol, 88%). The product was used without further purification for the investigation of its catalytic properties.

Spectroscopic data for **3**: Positive ion ESMS: $m/z = 585$ [Ru(η^6-$C_{10}H_{14}$)(pta)$_2$Cl]$^+$, 428 [Ru(η^6-$C_{10}H_{14}$)(pta)Cl]$^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -32.97$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 5.35$ (q, $J = 6.42$ Hz, 4H), 4.53 (s, 12H), 4.32 (s, 12H), 2.81 (septet, $J = 6.55$ Hz, 1H), 2.08 (s, 3H), 1.28 (d, $J = 6.55$ Hz, 6H); anal.: found (calcd.) C 38.03 (39.33) H 6.44 (5.70) N 11.81 (12.51).

Hydrogenation Reactions

All hydrogenations were carried out in a Parr stainless steel autoclave (300 mL) fitted with a PTFE liner. The catalyst was added directly to the autoclave and the solvent was added. The autoclave was then sealed and purged with nitrogen and the reaction substrate was then added through the liquid inlet port *via* a syringe. The autoclave was then purged thoroughly with hydrogen gas (99.9995% purity) and the appropriate reaction pressure was then set at room temperature. The autoclave was then heated to the required reaction temperature and stirring was commenced for the period required. Once the desired time period had elapsed, the stirring was stopped and the autoclave allowed to cool before releasing the pressure. Substrate and catalyst layers were separated in a separating funnel. In hydrogenations where colloidal poisoning was conducted 10 drops of mercury were added to the autoclave, otherwise all other parameters remained unchanged.

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