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Journal of Molecular Catalysis A: Chemical 204–205 (2003) 279–285

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Efficient catalytic hydration of acetonitrile to acetamide using $[Os(CO)_3Cl_2]_2$

Elena Cariati [a], Claudia Dragonetti [a], Luca Manassero [a], Dominique Roberto [a,*], Francesca Tessore [a], Elena Lucenti [b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano and Unità di Ricerca di Milano dell'INSTM, via Venezian 21, 20133 Milan, Italy*

[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM), Via C. Golgi 19, 20133 Milan, Italy*

Received 11 November 2002; received in revised form 31 January 2003; accepted 3 February 2003

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Various osmium species (e.g. $Na_2[Os_{10}C(CO)_{24}]$, $OsCl_3 \cdot nH_2O$ and $[Os(CO)_3Cl_2]_2$) are able to activate acetonitrile towards nucleophilic attack by water to give acetamide. The most efficient catalyst appears to be $[Os(CO)_3Cl_2]_2$, which gives good yields of acetamide by working in air at 76 °C. An increase of the quantity of water has a positive effect on yields, a plateau being reached with a molar ratio H_2O:CH_3CN of about 7.3:1. The catalytic activity of the osmium species decreases with prolonged heating, due to the progressive partial decarbonylation of *fac*-tricarbonylosmium(II) species. The complex $[Ru(CO)_3Cl_2]_2$ is much less efficient than its osmium analogue due to its easy conversion in $[Ru(CO)_2Cl_2(CH_3CN)_2]$ under the reaction conditions.

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Keywords: Hydration; Acetonitrile; Acetamide; Osmium; Hydrolysis

1. Introduction

Hydration of nitriles to give the corresponding carboxamides is an important reaction both from laboratory and industry point of view [1]. This reaction is catalyzed by various acids and bases, but many of these classical methods require harsh conditions and give low yields due to further hydrolysis of carboxamides into carboxylic acids (or their salts) [1–4]. The hydration of nitriles to amides may also be carried out using metals (such as copper) [5], working under neutral conditions. In order to obtain a high selectivity as well as good yields of carboxamides, in the last two decades, there has been increasing interest in the use of transition metal coordination catalysts which do not require extreme acidity and basicity [1,6–8]. Labile complexes served as catalysts whereas inert complexes allowed reactive intermediates to be trapped and gave kinetic and stereochemical information about the mechanisms of hydration [1]. Clearly, it appeared that coordination to various metal centers (e.g. ruthenium(II) [9,10], ruthenium(III) [9–11], cobalt(II) [12], cobalt(III) [10,13–17], rhodium(III) [9,10,18], iridium(III) [18], nickel(II) [12,19,20], palladium(II) [1,21–24], platinum(II) [25–29], copper(II) [12,19,20], and zinc(II) [19]) markedly enhances the

* Corresponding author. Tel.: +39-02-50314399; fax: +39-02-50314405.
E-mail address: dominique.roberto@unimi.it (D. Roberto).

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doi:10.1016/S1381-1169(03)00309-1

Table 1
Comparison of some catalysts and reaction conditions for the hydrolysis of acetonitrile at 80 ± 4 °C

Metal complex or salt	Molar ratio metal:CH_3CN[a]	Molar ratio H_2O:CH_3CN[a]	Time (h)	Yield (%)	Turnover frequency[b]	Turnover number[c]
$Pt(C_6H_8)(PPh_3)_2$[25]	1:957	1.2	16	6.1[d]	3.6[d]	58
$Pt(C_6H_9)(NHCOMe)(PPh_3)_2$[25]	1:957	1.2	5	3.7[d]	7[d]	35
$PtCH_3(NHCOMe)(PPh_3)_2$[25]	1:957	1.2	2.5	7.8[d]	30[d]	75
$PtC_6H_9(OH)(diphos)$[25]	1:957	1.2	1	0.7[d]	6.8[d]	6.8
$Pt(OH)Ph(PPh_3)_2$[26]	1:1600	0.6	20	4.8[d]	3.9[d]	77
$Pt(P(c\text{-}C_6H_{11})_3)_2$[26]	1:1600	0.6	20	33[d]	26[d]	520
$Pt(P(i\text{-}Pr)_3)_3$[26]	1:1600	0.6	20	25[d]	20[d]	405
$Pt(PEt_3)_3$[26]	1:1600	0.6	20	3.4[d]	2.7[d]	54
$Pt(NHCOMe)Ph(PPh_3)_2$[27]	1:1600	1	20	6.4[d]	5.1[d]	102[e]
$Pt(NHCOMe)Ph(PEt)_2$[27]	1:1600	1	20	10[d]	8.4[d]	169
$Pt(OH)Ph(PEt_3)_2$[27]	1:1600	1	20	11[d]	8.7[d]	173
$Pt(OH)Ph(P\text{-}t\text{-}Bu_2Me)_2$[27]	1:1600	1	20	1.4[d]	1.1[d]	22
$[PtH(H_2O)(PMe_3)_2][OH]$[28]	1:478	2.9	–	–	178	6000
$[PtH(PMe_2OH)(Pme_2O)_2H]$[8]	1:6486	1.4	15.5[f]	91	380	5700
$PdCl(OH)(bipy)(H_2O)$[21]	1:383	6	3	23	29[d]	88[d]
$PdCl(OH)(bipy)(H_2O)$[21]	1:383	6	24	59	9[d]	226[d]
$PdCl(OH)(bipy)(H_2O)$[21]	1:383	6	48	67.5	5.4[d]	259[d]
trans-$Ir(OH)(CO)(PPh_3)_2$[25]	1:957	1.2	20	2.6[d]	1.2[d]	25
trans-$Rh(OH)(CO)(PPh_3)_2$[25]	1:957	1.2	3	16[d]	50[d]	150

[a] Initial molar ratio.
[b] mol/(mol of metal h).
[c] mol/(mol of metal).
[d] Calculated from reported data.
[e] When experiment was repeated with a fresh charge of acetonitrile:water under identical conditions using recovered catalyst, only 22 mol acetamide per mol catalyst was obtained.
[f] Working at 90 °C.

rates of hydrolysis of organonitriles to the corresponding coordinated carboxamides. A lot of work was dedicated to examine the efficiency (in terms of carboxamide yield or turnover frequency "(mol carboxamide)/(mol of metal h)" or turnover number "(mol carboxamide)/(mol of metal)") of metal transition complexes as catalysts for nitrile hydration. However, although the catalytic activity of metal complexes from group 11 (e.g. copper(II) [12]), group 10 (e.g. nickel(II) [12], palladium(II) [1,21–24] and platinum(II) [8,25–28]; see Table 1 in the case of acetonitrile) and group 9 (e.g. cobalt(II) [12], rhodium(I) [25] and iridium(I) [25]; see Table 1 in the case of acetonitrile) has been well investigated, to our knowledge no report appeared on the efficiency of group 8 transition metal carbonyl complexes as catalysts for hydration of nitriles.

However, a few years ago in Professor Ugo's laboratory, it was observed that extraction with acetonitrile of silica-supported $Na_2[Os_{10}C(CO)_{24}]$, formed by reduction (1 atm H_2, 200 °C) of silica-supported $[Os(CO)_3Cl_2]_2$ in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1), gives some acetamide [30]. We were curious to know: (i) the efficiency of $Na_2[Os_{10}C(CO)_{24}]$ as catalyst for this hydration reaction; (ii) whether silica and Na_2CO_3 played a significant role in this catalysis; and (iii) the efficiency of other osmium and related ruthenium species. Therefore, we investigated the use of various osmium and ruthenium species ($Na_2[Os_{10}C(CO)_{24}]$, $[M(CO)_3Cl_2]_2$ and $MCl_3{\cdot}nH_2O$ where M = Ru, Os) as potential catalysts for the hydration of acetonitrile. The results of this study, which reveals the particular efficiency of $[Os(CO)_3Cl_2]_2$, are reported in this paper.

2. Experimental

2.1. General comments

$Na_2[Os_{10}C(CO)_{24}]$ [30], $[Ru(CO)_3Cl_2]_2$ [31] and $[Os(CO)_3Cl_2]_2$ [32] were prepared according to the

literature whereas hydrated metal salts were commercially available from Engelhard ($RuCl_3 \cdot nH_2O$, 39.95% Ru; $RhCl_3 \cdot nH_2O$, 40.93% Rh; $IrCl_3 \cdot nH_2O$, 52.14% Ir) or Strem Chemicals ($OsCl_3 \cdot nH_2O$, 53.7% Os). Acetonitrile (HPLC grade) was purchased from Aldrich and used without further purification.

2.2. Catalytic hydration of acetonitrile by silica-supported $Na_2[Os_{10}C(CO)_{24}]$

Silica-supported $Na_2[Os_{10}C(CO)_{24}]$ was prepared as previously reported by the reduction of $[Os(CO)_3Cl_2]_2$ supported on a silica surface added with Na_2CO_3 (2 wt.% Os:SiO_2; molar ratio Na_2CO_3:Os = 10:1) under 1 atm of H_2 at 200 °C for 24 h [30]. This resulting silica powder, after washing with dichloromethane to remove traces of $[H_4Os_4(CO)_{12}]$ and $Na[H_3Os_4(CO)_{12}]$ [30], was treated with a mixture of acetonitrile and water (molar ratios Os:CH_3CN = 1:1150; H_2O:CH_3CN = 1.5:1) for 72 h at 25 °C. Evaporation of the solvents followed by extraction of the resulting silica powder with dichloromethane afforded acetamide (0.31 g; 5.2 mmol; 0.7% yield).

2.3. Catalytic hydration of acetonitrile by a metal complex in solution

Typically, in a one-neck flask equipped with a condenser and a magnetic stirring bar, a solution of a given complex ($Na_2[Os_{10}C(CO)_{24}]$, $[M(CO)_3Cl_2]_2$, where M = Ru, Os, or $MCl_3 \cdot nH_2O$, where M = Ru, Os, Rh or Ir) in a mixture of acetonitrile and water was stirred at room temperature or under reflux (76 °C). The various molar ratios metal:acetonitrile and water:acetonitrile used are given in Table 2. In one experiment with $[Os(CO)_3Cl_2]_2$, NaOH (molar ratio NaOH:Os = 1:1) was added to the reaction mixture

Table 2
Comparison of various catalysts and reaction conditions studied in this work for the hydrolysis of acetonitrile

Metal complex or salt	Molar ratio metal:CH_3CN[a]	Molar ratio H_2O:CH_3CN[a]	Time (h)	Yield (%)	T (°C)	Turnover frequency[b]	Turnover number[c]
$Na_2[Os_{10}C(CO)_{24}]/SiO_2$[d]	1:1150	1.5	72	0.7	25	0.1	8
$Na_2[Os_{10}C(CO)_{24}]$	1:1150	1.5	72	0.3	25	0.04	3
$Na_2[Os_{10}C(CO)_{24}]$	1:1150	1.5	12	1.3	76[e]	1.3	15
$[Os(CO)_3Cl_2]_2$	1:1150	1.5	12	6.3	76[e]	6	72
$[Os(CO)_3Cl_2]_2$	1:1150	1.5	48[f]	9.2	150	2.2	106
$[Os(CO)_3Cl_2]_2$	1:300	1.5	22	15	76[e]	2.0	45
$[Os(CO)_3Cl_2]_2$	1:300	2.9	22	27	76[e]	3.6	80
$[Os(CO)_3Cl_2]_2$ + NaOH[g]	1:300	2.9	22	25	76[e]	3.4	75
$[Os(CO)_3Cl_2]_2$	1:300	7.3	3	8.2	76[e]	8.2	25
$[Os(CO)_3Cl_2]_2$	1:300	7.3	12	26	76[e]	6.5	78
$[Os(CO)_3Cl_2]_2$	1:300	7.3	22	33[h]	76[e]	4.5	98
$[Os(CO)_3Cl_2]_2$	1:300	7.3	44	44	76[e]	3	132
$[Os(CO)_3Cl_2]_2$	1:300	15	22	34	76[e]	4.6	102
$OsCl_3 \cdot nH_2O$	1:300	1.5	22	4.3	76[e]	0.6	13
$[Ru(CO)_3Cl_2]_2$	1:300	1.5	22	0.2	76[e]	0.02	0.5
$RuCl_3 \cdot nH_2O$	1:300	1.5	22	3.4	76[e]	0.5	10
$RhCl_3 \cdot nH_2O$	1:300	1.5	22	0	76[e]	0	0
$IrCl_3 \cdot nH_2O$	1:300	1.5	22	0.5	76[e]	0.07	1.5

[a] Initial molar ratio.
[b] mol/(mol of metal h).
[c] mol/(mol of metal).
[d] In the presence of Na_2CO_3[30].
[e] Reflux temperature of the azeotrope.
[f] Under 500 kPa of N_2.
[g] Molar ratio NaOH:Os = 1:1.
[h] When experiment was repeated with a fresh charge of acetonitrile:water under identical conditions using recovered catalyst, the yield in acetamide was 18% only.

(see Table 2) whereas another experiment was carried out in an autoclave working at 150 °C under 500 kPa of N_2. In all the cases, after cooling, solvents were removed on a rotary evaporator, and acetamide was sublimed at ca. 60 °C/133 Pa as previously reported [27]. In some experiments, the residue after sublimation was examined by IR and NMR spectroscopies and re-used with fresh acetonitrile and water.

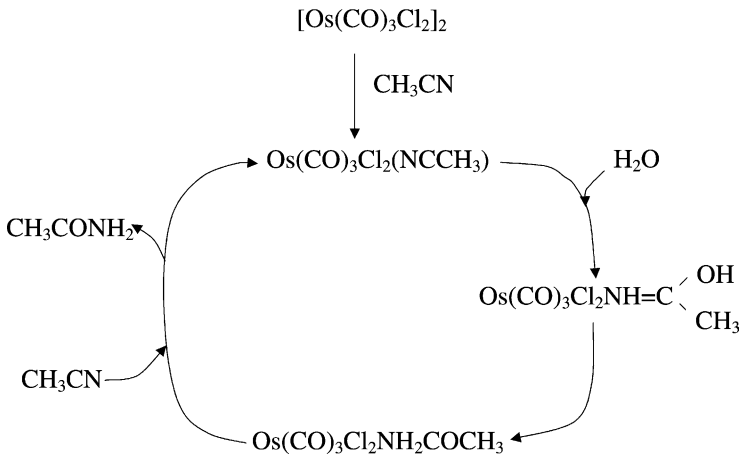
3. Results and discussion

When silica-supported $Na_2[Os_{10}C(CO)_{24}]$, prepared as above reported [30], is treated with a mixture of acetonitrile and water (molar ratios Os:CH_3CN = 1:1150; H_2O:CH_3CN = 1.5:1) for 72 h at 25 °C, some acetamide is formed. Evaporation of the solvent followed by extraction of the resulting silica powder with dichloromethane affords this carboxamide in 0.7% yield only. A similar low yield (0.3%) was obtained by stirring a solution of $Na_2[Os_{10}C(CO)_{24}]$ in acetonitrile and water under the same reaction conditions but in the absence of silica and Na_2CO_3, suggesting that the latter do not play a significant role in the catalytic process, whereas a slightly higher yield (1.3%) could be reached by working at reflux temperature (76 °C, the boiling point of the azeotrope water:acetonitrile) for 12 h (Table 2). At the end of the reaction, the starting cluster $Na_2[Os_{10}C(CO)_{24}]$ was recovered. These preliminary results prompted us to test the efficiency of other osmium and related ruthenium species ($[M(CO)_3Cl_2]_2$ and $MCl_3{\cdot}nH_2O$ with M = Ru, Os) for the hydration of nitrile to give acetamide working under reflux without added silica or sodium carbonate (Table 2).

It turned out that $[Os(CO)_3Cl_2]_2$ is much more efficient than $Na_2[Os_{10}C(CO)_{24}]$. In fact by stirring a solution of $[Os(CO)_3Cl_2]_2$ in acetonitrile and water (same molar ratios Os:CH_3CN = 1:1150; H_2O:CH_3CN = 1.5:1) for 12 h at 76 °C, acetamide is formed in 6.3% yield. The salt $OsCl_3{\cdot}nH_2O$ (where Os(III) has a $5d^5$ electronic configuration) is somewhat less efficient than the Os(II) complex (with a $5d^6$ electronic configuration), a lower yield (4.3%) being obtained even by working with a higher quantity of osmium (molar ratio Os:CH_3CN = 1:300) for a longer reaction time (22 h). Under the latter reaction conditions, $RuCl_3{\cdot}nH_2O$ (Ru(III) has a $4d^5$ electronic configuration) has an effectiveness slightly lower than its osmium analogue (3.4% yield) whereas $[Ru(CO)_3Cl_2]_2$ (Ru(II) has a $4d^6$ electronic configuration) is not a good catalyst (0.2% yield). In order to verify whether the major extension of the d orbitals in the osmium species could contribute to their higher efficiency with respect to the related ruthenium species, the salts $RhCl_3{\cdot}nH_2O$ and $IrCl_3{\cdot}nH_2O$, where Rh(III) and Ir(III) have a $4d^6$ and $5d^6$ electronic configuration respectively, were investigated (Table 1). No acetamide is formed by using $RhCl_3{\cdot}nH_2O$, whereas a 0.5% yield is obtained with $IrCl_3{\cdot}nH_2O$, confirming, for a given coordination sphere, a slightly higher efficiency of the third metal transition period with respect to the second. However, the large difference in the effectiveness of $[Os(CO)_3Cl_2]_2$ with respect to $[Ru(CO)_3Cl_2]_2$ cannot be attributed to this effect only, as explained below.

In the case of $[Os(CO)_3Cl_2]_2$, a reasonable mechanism (Scheme 1) would involve first cleavage of the dimeric complexes to give $[Os(CO)_3Cl_2(NCCH_3)]$ (we observed, monitoring by infrared spectroscopy in chloroform, that the chloro bridge of these complexes is cleaved much more rapidly by CH_3CN than by water) which would undergo an external attack by water to give $[Os(CO)_3Cl_2(NH{=}C(OH)CH_3)]$ followed by tautomeric rearrangement of the iminol into amide $[Os(CO)_3Cl_2(NH_2COCH_3)]$ and release of the acetamide. Such a mechanism has been proposed in the case of the diethylenetriamine palladium(II) complex [1].

The much lower effectiveness of $[Ru(CO)_3Cl_2]_2$ can be attributed to its easy conversion into $[Ru(CO)_2Cl_2(CH_3CN)_2]$ under the reaction conditions. In this complex, acetonitrile is coordinated to a less acidic metal center (having two COs and one nitrile instead of three COs) and therefore is less easily attacked by a nucleophile like water. In agreement with this hypothesis we found that $[Ru(CO)_3Cl_2]_2$ is easily converted to the known complex $[Ru(CO)_2Cl_2(CH_3CN)_2]$ by refluxing in acetonitrile [33,34]. After 10 min a mixture of *fac*-$[Ru(CO)_3Cl_2(CH_3CN)]$ [33,35] (ν_{CO} in CH_3CN = 2143(s), 2082(s), 2069(s) cm^{-1}) and $[Ru(CO)_2Cl_2(CH_3CN)_2]$ (ν_{CO} in CH_3CN = 2081(s), 2020(s) cm^{-1}) is present whereas after 1 h there is only the dicarbonyl species. On the contrary, only *fac*-$[Os(CO)_3Cl_2(CH_3CN)]$ (ν_{CO} in CH_3CN = 2134(s), 2059(s), 2041(s) cm^{-1}) is formed by reflux-



Scheme 1. Possible mechanism for the conversion of acetonitrile to acetamide by $[Os(CO)_3Cl_2]_2$.

ing a solution of $[Os(CO)_3Cl_2]_2$ in acetonitrile for 1 h. The lower tendency of the dichloroosmium(II) carbonyl complex to lose CO in comparison to its ruthenium analogue is well known [36].

It is worth pointing out that the important role played by electron-withdrawing ancillary ligands such as carbonyls is confirmed by the much higher efficiency of $[Os(CO)_3Cl_2]_2$ with respect to $OsCl_3 \cdot nH_2O$ and $IrCl_3 \cdot nH_2O$ where the metal center has a higher formal oxidation state. Besides, as above reported, osmium and iridium species display a better efficiency than related ruthenium and rhodium species. This behavior is in contrast with the worst efficiency of *trans*-$[Ir(OH)(CO)(PPh_3)_2]$ ($5d^8$) with respect to *trans*-$[Rh(OH)(CO)(PPh_3)_2]$ ($4d^8$) [25] (Table 1), but this difference can be reasonably attributed to the different mechanism that involves, for the latter complexes, an internal attack by the OH ligand instead of an external attack by water. Thus, for *trans*-$[M(OH)(CO)(PPh_3)_2]$ (M = Rh, Ir), the hydration reaction involves insertion of the nitrile into the M–OH bond to give an N-bonded imino-alcohol complex [MN=C(OH)R] which rearranges to the N-amido complex [MNHCOR]; addition of water to the latter regenerates the M–OH bond, liberating acetamide [25].

3.1. $[Os(CO)_3Cl_2]_2$ as catalyst

The particular efficiency of $[Os(CO)_3Cl_2]_2$ for the hydration of acetonitrile (6.3% yield by working at 76 °C for 12 h with molar ratios $Os:CH_3CN = 1:1150$; $H_2O:CH_3CN = 1.5:1$) prompted us to study for this catalyst the effect of: (i) the temperature; (ii) the quantity of osmium; (iii) the quantity of water; and (iv) the reaction time (Table 2).

The use of a higher temperature (150 °C instead of 76 °C, working under 500 kPa of N_2) does not lead to a significant effect, the acetamide being obtained in 9.2% yield after 48 h.

On the other hand, an increase of the quantity of osmium led to better yields. Thus, by stirring a solution of $[Os(CO)_3Cl_2]_2$ with acetonitrile and water (molar ratios $Os:CH_3CN = 1:300$; $H_2O:CH_3CN = 1.5:1$) for 22 h under reflux, acetamide is obtained in 15% yield evidencing in this particular case that an increase of the quantity of osmium by a factor of 3.8 leads to an increase of the yield by a factor of 2.4.

It is worth pointing out that, in some cases, hydration of acetonitrile by a metal complex requires the presence of a base which may allow the formation of a metal–OH bond [21]. For example, by working with an acetonitrile:water solution of $[PdCl_2(bipy)]$ (molar ratio $palladium:CH_3CN:H_2O = 1.2:230:690$) under reflux, no acetamide is formed in the absence of a base whereas in the presence of NaOH, which allows the formation of the active catalyst [PdCl(OH)(bipy)], it is obtained in 20% yield for 24 h [21]. However, in our catalytic system, the addition of one equivalent of NaOH per osmium, which leads to the substitution of one chloro ligand by an hydroxo ligand [36], has no effect (see Table 2).

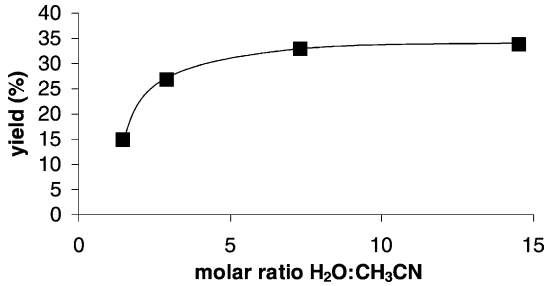


Fig. 1. Yield with respect to molar ratio $H_2O:CH_3CN$, after 22 h with an initial molar ratio osmium:CH_3CN = 1:300.

Remarkably, it appeared that an increase of the quantity of water leads to much better yields, a plateau being reached with a molar ratio $H_2O:CH_3CN$ of about 7.3:1 (Fig. 1). This is an interesting observation because the effect of the quantity of water on the hydration of nitriles is usually not investigated in the literature. Only in the cases of the hydration of $CHCl_2CN$ and CH_3CN by *cis*-[Pd(ethylenediamine)$(H_2O)_2]^{2+}$ [1] and $[PtH(H_2O)(PMe_3)_2][OH]$ [28], respectively, it was reported that the rate constant increases by increasing the quantity of water.

By working under reflux with molar ratios Os:CH_3CN = 1:300 and $H_2O:CH_3CN$ = 7.3:1, we found that acetamide is formed in 8.2, 26, 33 and 44% yields after 3, 12, 22 and 44 h, respectively (Fig. 2).

Clearly, the catalytic activity of the osmium species decreases with prolonged heating, due to the progressive partial decarbonylation of *fac*-tricarbonylosmium(II) species into mixtures of still unidentified complexes as evidenced by infrared spectroscopy. After 3 h, the osmium containing residue dissolved in dichloromethane shows two carbonyl bands at 2123(m) and 2030(s) cm^{-1}, similar to those of *fac*-$[Os(CO)_3Cl_2(H_2O)]$ obtained by reaction of $[Os(CO)_3Cl_2]_2$ with water in dichloromethane, and reacts with aqueous HCl to give *fac*-$[Os(CO)_3Cl_3]^-$ [36]. After 12 and 22 h, these two carbonyl bands are still present in the osmium residue but along with other carbonyl bands at 2070(w), 2047(s), 1981(s) cm^{-1}. After 44 h, only weak carbonyl bands are present at 2070(w), 2008(w), 1977(w) cm^{-1}, evidencing the absence of tricarbonyl osmium species.

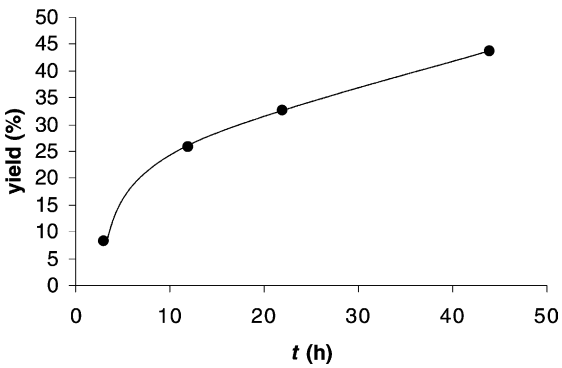


Fig. 2. Yield with respect to reaction time, by using molar ratios osmium:CH_3CN = 1:300 and $H_2O:CH_3CN$ = 7.3:1.

Interestingly, when the osmium-containing residue obtained after reaction for 22 h and successive removal of water, acetonitrile and acetamide is re-used with a fresh charge of acetonitrile and water, acetamide is formed in 18% yield after refluxing for 22 h (Table 2), evidencing that the recovered osmium species are less active than the starting $[Os(CO)_3Cl_2]_2$ complex which afforded a 33% yield under similar conditions. However, it is interesting to note that the yield (18%) obtained after 22 h by using this recovered catalyst with a fresh charge of reagents is higher than that formed without removal of the acetamide (44% after 44 h − 33% after 22 h = 11% yield) suggesting that there could be some inhibiting effect due to the presence of acetamide as previously observed for some platinum(II) complexes [28].

4. Conclusion

Although $Na_2[Os_{10}C(CO)_{24}]$ catalyzes the hydration of acetonitrile, an interesting example of a cluster acting as a catalyst, it appeared that $[Os(CO)_3Cl_2]_2$ is much more efficient. Remarkably, for this hydration reaction, the catalytic activity for the latter is higher than that for *trans*-$[Ir(OH)(CO)(PPh_3)_2]$ [25] and various platinum complexes [25,26] and similar to that reported for many platinum and palladium complexes [21,25–27] under conditions quite similar to ours (see Tables 1 and 2). However, it fails to approach that of $[PtH(H_2O)(PMe_3)_2][OH]$ [28], $[PtH(PMe_2OH)(PMe_2O)_2H]$ [8] and *trans*-$[Rh(OH)(CO)(PPh_3)_2]$ [25], although it has the advantage of being easily prepared, easily handled and not air-sensitive contrarily to most platinum complexes for nitrile hydration which should be used working under nitrogen [26–28].

Therefore, these preliminary results on the use of osmium species for nitrile hydration are promising and, as an extension of this study, it would be of particular interest to examine the hydration of more complex nitriles such as acrylonitrile or crotonitrile where the selectivity is often not excellent, mixtures of products being obtained even using various platinum species as catalysts [25–27]. Finally, this work points out that surface-mediated syntheses can be not only a spring of inspiration for more convenient syntheses in solution [37], but the study of the surface organometallic chemistry involved can also lead to the discovery of new homogeneous catalysts.

Acknowledgements

We wish to thank deeply Professor Renato Ugo for his incomparable guidance during our scientific growth. This work was supported by the Ministero dell'Istruzione, dell'Università e della Ricerca and by the Consiglio Nazionale delle Ricerche.

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