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LETTER

Osmium carbonyl cluster based catalysts for selective hydrogenation of α, β-unsaturated carbonyl compounds

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Although ruthenium complexes feature extensively in homogeneous catalytic reactions [1], applications of osmium complexes to homogeneous catalysis have been less frequently reported. In fact a number of stable osmium complexes have been isolated to serve as models for catalytic intermediates in catalytic reactions by taking advantage of the kinetically inert character of low-valent osmium [2]. A few mononuclear osmium complexes are known to be active catalysts for C=C bond migration, isomerization of allyl alcohol, hydrogenation of acyclic and cyclic olefins, dienes, acetylenes, aldehydes, ketones, α, β-unsaturated aldehydes and ketones, and for hydroformylation of alkenes [3]. Triosmium dodecacarbonyl has been shown to be active in alkene isomerization [4], alkyne cyclotrimerization [5], C–N bond activation [6], hydroformylation [6], water-gas shift [7, 8] and CO hydrogenation [9] reactions. The dihydrido cluster, $H_2Os_3(CO)_{10}$, has been reported to hydrogenate olefins in solution [10] and supported in silica [11]. Sanchez-Delgado *et al.* discovered that a number of tri- and tetra-nuclear osmium clusters with coordinately unsaturated or 'open' structures can effectively hydrogenate carbon–carbon double bonds under moderate reaction conditions [12].

Recently we reported that $Ru_3(CO)_{12}$-based systems are effective catalysts for the selective hydrogenation of α, β-unsaturated aldehydes [13], therefore we are interested in studying the catalytic activities of the analogous osmium systems for similar reactions. Here we present the results of our work aimed at utilizing the $Os_3(CO)_{12}$-based systems for the homogeneous selective hydrogenation of α, β-unsaturated carbonyl compounds.

Experimental

Reagent grade toluene, xylene and mesitylene were distilled over sodium benzophenone under nitrogen. Cinnamaldehyde (Aldrich) was stored over a molecular sieve and vacuum distilled before use. Benzylideneacetone (Merck) was recrystallized from propan-2-ol. Crotonaldehyde (Merck) and cyclohex-1-en-2-one (Aldrich) were stored over a molecular sieve and distilled before use. Triphenylphosphine (Aldrich) was recrystallized from ethanol; tributylphosphine and triphenyl phosphite were distilled under vacuum. High purity hydrogen (Hong Kong Oxygen) was used directly. Triosmium dodecacarbonyl was obtained commercially and was used directly; $H_2Os_3(CO)_{10}$ [14] and $H_4Os_4(CO)_{12}$ [12] were prepared by reported procedures.

Hydrogenation reaction

All reactions were carried out in a 100 ml stainless steel autoclave. In a typical run, ~30 mg of the osmium cluster, 20 ml of solvent, 2.0–2.5 g substrate and the appropriate amount of phosphine or phosphite were mixed in the autoclave. After flushing with H_2 three times, the system was heated with stirring at 140 °C under 45 atm. of hydrogen. At the end of the desired time, the reactor was cooled rapidly and the reaction mixture was analyzed by gas chromatography on a Perkin-Elmer Sigma 3B apparatus equipped with a FID. A 25 m×0.32 mm OV-1 capillary column was used for the hydrogenation products of cinnamaldehyde and benzylideneacetone, and a 50 m×0.32 mm OV-17 capillary column was used for that of crotonaldehyde and cyclohex-1-en-2-one.

Results and discussion

In Table 1 are reported the results obtained in the hydrogenation of two α, β-unsaturated aldehydes, crotonaldehyde and cinnamaldehyde, respectively.

Triosmium dodecacarbonyl by itself is not a very satisfactory catalyst for selective hydrogenation of α, β-unsaturated aldehydes. Addition of one equivalent of triphenylphosphine or triphenyl phosphite does not enhance the activity in the case of cinnamaldehyde, although some increase in activity is observed in the reduction of crotonaldehyde. Addition of the more basic tributylphosphine generates very effective catalyst systems (runs 2, 3, 9 and 10 in Table 1), giving the unsaturated alcohols as the predominant products. Sim-

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TABLE 1. Hydrogenation of α, β-unsaturated aldehydes[a]

Run	Catalyst system	Conversion[b] (%)	Unsaturated alcohol (%)	Saturated aldehyde (%)	Saturated alcohol (%)
Substrate: crotonaldehyde					
1	$Os_3(CO)_{12}$	18	13	5	
2	$PBu^n_3/Os_3(CO)_{12}$ (1/1)	93	67		26
3	$PBu^n_3/Os_3(CO)_{12}$ (15/1)	93[c]	89		4
4	$PPh_3/Os_3(CO)_{12}$ (1/1)	31	18	9	4
5	$PPh_3/Os_3(CO)_{12}$ (15/1)	47	35	4	8
6	$P(OPh)_3/Os_3(CO)_{12}$ (1/1)	27	17	3	7
7	$P(OPh)_3/Os_3(CO)_{12}$ (15/1)	28	9		19
Substrate: cinnamaldehyde					
8	$Os_3(CO)_{12}$	15	7	6	2
9	$PBu^n_3/Os_3(CO)_{12}$ (1/1)	57	40	10	7
10	$PBu^n_3/Os_3(CO)_{12}$ (15/1)	97	86		11
11	$PPh_3/Os_3(CO)_{12}$ (1/1)	12	6	5	1
12	$PPh_3/Os_3(CO)_{12}$ (15/1)	98	91	1	6
13	$P(OPh)_3/Os_3(CO)_{12}$ (1/1)	15	7	6	2
14	$P(OPh)_3/Os_3(CO)_{12}$ (15/1)	81	79	1	1
15	$H_4Os_4(CO)_{12}$[d]	10	5	3	2
16	$PPh_3/H_4Os_4(CO)_{12}$ (20/1)[d]	5	2	1	2
17	$H_2Os_3(CO)_{10}$	44	24	11	9
18	$PPh_3/H_2Os_3(CO)_{10}$ (15/1)	8	2	3	3

[a] Reaction conditions: 3.3×10^{-2} mmol osmium cluster + n equivalents phosphine or phosphite ($n = 0$, 1 or 15) + 20.5 mmol substrate in 20 ml solvent (mesitylene for crotonaldehyde; xylene for cinnamaldehyde), H_2 pressure 45 atm.; temperature 140 °C; reaction time, 9 h for crotonaldehyde, 7 h for cinnamaldehyde. [b] Based on substrate used. [c] Reaction time 3 h. [d] 2.5×10^{-2} mmol $H_4Os_4(CO)_{12}$ used.

ilar results are also observed when excess of triphenylphosphine or triphenylphosphite is added to $Os_3(CO)_{12}$ in the reduction of cinnamaldehyde (runs 12 and 14 in Table 1). In our recent report on the $Ru_3(CO)_{12}$-based catalysts for selective hydrogenation of α, β-unsaturated aldehydes [13], strong dependency of selectivity on the $P/Ru_3(CO)_{12}$ ratio was observed. When the $P/Ru_3(CO)_{12}$ ratio was 1/1, the olefinic functions of α, β-unsaturated aldehydes were preferentially reduced, but increase of the $P/Ru_3(CO)_{12}$ ratio led to selective hydrogenation of the carbonyl groups, giving the unsaturated alcohols as the predominant products. Similar dependency of selectivity on the phosphine/complex ratio was also observed in the iridium phosphine systems [15]. But our present $Os_3(CO)_{12}$-based catalyst systems do not show such selectivity dependency on the $P/Os_3(CO)_{12}$ ratio.

Triosmium dodecacarbonyl reacts readily with H_2 at atmospheric pressure and elevated temperature to give the electron deficient cluster, $H_2Os_3(CO)_{10}$ [14]; and the tetranuclear cluster, $H_4Os_4(CO)_{12}$ can be prepared in quantitative yield at 150 °C and 15 atm. H_2 [12]. The catalytic activities of the $H_2Os_3(CO)_{10}$- and $H_4Os_4(CO)_{12}$-based systems (runs 15–18, Table 1) were investigated. Comparison of the results of the $PPh_3/H_4Os_4(CO)_{12}$ (20/1) and $PPh_3/H_2Os_3(CO)_{10}$ (15/1) systems with that of $PPh_3/Os_3(CO)_{12}$ (15/1) indicates that the two hydrido cluster systems fail to generate the highly active species for the hydrogenation reactions. It is not surprising to find that $H_2Os_3(CO)_{12}$ alone (run 17, Table 1) is a relatively active system because it is well known that this formally electron deficient cluster compound is much more reactive than the saturated cluster, $Os_3(CO)_{12}$ toward olefines and acetylenes [10]. Addition of excess triphenylphosphine to $H_2Os_3(CO)_{10}$ (run 18, Table 1) probably results in the formation of the much less reactive adduct $H_2Os_3(CO)_{10}PPh_3$ [16].

The influence of reaction temperature on the activity of the $PPh_3/Os_3(CO)_{12}$ (15/1) system in the hydrogenation of cinnamaldehyde was studied. At temperatures below 130 °C, yields of products were low, but at 130 °C there was a dramatic increase in catalytic activity. The optimal temperature was found to be 140 °C. The effect of hydrogen pressure on activity was also studied. It was found that under atmospheric pressure of H_2, the $PPh_3/Os_3(CO)_{12}$ (15/1) system was inactive. At 30 atm., conversion jumped to 50% and at 45 atm. or above, the conversion was near quantitative.

Table 2 show the results of hydrogenation of benzylideneacetone and cyclohex-1-en-2-one. Although the $Os_3(CO)_{12}$-based systems preferentially catalyze reduction of the carbonyl functions of α, β-unsaturated

TABLE 2. Hydrogen of α, β-unsaturated ketones[a]

Run	Catalyst system	Conversion[b] (%)	Unsaturated alcohol (%)	Saturated ketone (%)	Saturated alcohol (%)
Substrate: benzylideneacetone					
1	$Os_3(CO)_{12}$	26	1	24	1
2	$PBu^n_3/Os_3(CO)_{12}$ (1/1)	99		67	32
3	$3PBu^n_3/Os_3(CO)_{12}$ (15/1)	98		63	35
4	$PPh_3/Os_3(CO)_{12}$ (1/1)	26	1	24	1
5	$PPh_3/Os_3(CO)_{12}$ (15/1)	17	2	9	6
6	$P(OPh)_3/Os_3(CO)_{12}$ (1/1)	35	2	32	1
7	$P(OPh)_3/Os_3(CO)_{12}$ (15/1)	7		6	1
Substrate: cyclohex-1-en-2-one					
8	$Os_3(CO)_{12}$	46	5	33	8
9	$PBu^n_3/Os_3(CO)_{12}$ (1/1)	81	1	51	29
10	$PBu^n_3/Os_3(CO)_{12}$ (15/1)	70	2	44	24
11	$PPh_3/Os_3(CO)_{12}$ (1/1)	50	2	35	13
12	$PPh_3/Os_3(CO)_{12}$ (15/1)	14	1	10	3
13	$P(OPh)_3/Os_3(CO)_{12}$ (1/1)	45	3	30	12
14	$P(OPh)_3/Os_3(CO)_{12}$ (15/1)	10	1	5	4

[a] Reaction conditions: 3.3×10^{-2} mmol $Os_3(CO)_{12}+n$ equivalents phosphine or phosphite ($n=0.1$ or 15) + 16.5 mol benzylideneacetone in 20 ml xylene or 20.7 mmol cyclohex-1-en-2-one in 20 ml toluene; H_2 pressure 45 atm.; temperature 140 °C; reaction time, 9 h for benzylideneacetone, 7 h for cyclohex-1-en-2-one. [b] Based on substrate used.

aldehydes, they show high selectivity toward reduction of the carbon–carbon double bonds of α, β-unsaturated ketones. Triosmium dodecacarbonyl alone shows moderate activities in the hydrogenation reactions of benzylideneacetone and cyclohex-1-en-2-one. No marked improvement in activity is observed when triphenylphosphine or triphenylphosphite is used as additive. In fact, % conversion decreases when excess of either additive is used. Addition of the more basic tributylphosphine generates very effective catalyst systems for hydrogenation reactions (runs 2, 3, 9 and 10, Table 2).

We attempted to gain some information about the composition of the osmium-containing products after the hydrogenation of cinnamaldehyde with $PPh_3/Os_3(CO)_{12}$ (15/1). It was found that the osmium-containing products after catalysis are a very complex mixture and we are now trying to separate the components in the mixture by chromatographic methods. The complexity of the reaction mixture is not unexpected since it is known that $Os_3(CO)_{12}$ easily undergoes substitution reactions with phosphines [17], and oxidation-addition products are readily formed from reactions of $Os_3(CO)_{12}$ with α, β-unsaturated aldehydes or ketones [18].

In summary, our present work demonstrates that the $Os_3(CO)_{12}$-based systems are very effective in catalyzing selective hydrogenation of α, β-unsaturated aldehydes and ketones. Further work in this area is in progress.

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