Bromocarbonylhydridotris(triphenylphosphine)osmium(II): a Versatile Catalyst for Homogeneous Organic Reactions.

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The title compound has been found to be an efficient catalyst for C=C bond migration, hydrogenation of acyclic and cyclic olefins, aldehydes, ketones, and α,β-unsaturated aldehydes, and for hydroformylation of hex-1-ene under moderate reaction conditions.

Although first and second row group 8 metal complexes feature extensively in homogeneous catalytic reactions,[1] few examples are known of active catalysts derived from their third row congeners. In the case of osmium, the catalytic behaviour of $Os_3(CO)_{12}$ in alkene isomerisation[2] and hydrogenation,[3] alkyne cyclotrimerisation,[4] C–N bond activation,[5] hydroformylation,[6] and in the water-gas shift[6,7] and CO hydrogenation[8] reactions in solution has been investigated. For mononuclear complexes, however, the only reported examples of catalytic reactions briefly deal with C=C bond hydrogenation by the use of $OsHCl(CO)(PPh_3)_3$,[9] $OsH_2(CO)(PEtPh_2)_3$,[10] $OsHCl(PPh_3)_3$,[11] $OsH_3(PPh_3)_3$,[11] and $OsHCl_2(AsPh_3)_3$.[11]

We now report a variety of organic reactions (Table 1) that can be efficiently catalysed by a mononuclear osmium(II) complex, namely $OsHBr(CO)(PPh_3)_3$ (**1**), which is easily prepared (and also commercially available)[12] and highly stable to oxygen, moisture, and elevated temperatures.

Hex-1-ene is rapidly isomerised by a solution of (**1**) in toluene at 150 °C under N_2 or Ar to an equilibrium mixture of hex-2-enes, whilst no C=C bond migration to the 3-position is observed. Under dihydrogen at atmospheric pressure, hydrogenation to n-hexane is observed together with the formation of hex-2-enes, which are more slowly reduced to the alkane; cyclohexene is not hydrogenated at 1 atm, but rapid conversion into cyclohexane is achieved under 5 atm of H_2.

Propionaldehyde and acetone can also be catalytically hydrogenated by (**1**) to their corresponding alcohols as the sole products under moderate reaction conditions at rates comparable to those reported by us for the same reactions using analogous ruthenium complexes;[13] this represents, to our knowledge, the first example of an osmium-catalysed homogeneous hydrogenation of the carbonyl group.

α,β-Unsaturated aldehydes, as exemplified by crotonaldehyde, may be hydrogenated to the saturated aldehyde, the unsaturated alcohol, or the fully reduced product, the relative proportions being dependent on the reaction conditions. As shown in Table 1, at 150 °C and 5 atm of H_2 the main product obtained is n-butanol, but at 100 °C and 1 atm of H_2, a 1:1 mixture of but-2-en-1-ol and butyraldehyde is produced, whilst no n-butanol is observed.

Table 1. Homogeneous catalysis by $OsHBr(CO)(PPh_3)_3$ in toluene at 150 °C unless otherwise noted.[a]

Reactants	P/ atm	t/ min	% Conversion	Product Distribution (%)
Hex-1-ene	—	30	95	*cis*-Hex-2-ene (27) *trans*-Hex-2-ene (73)
Hex-1-ene + H_2	1	30	95	*cis*-Hex-2-ene (19) *trans*-Hexene (45) n-Hexane (36)
Cyclohexene + H_2	1	60	—	No reaction
Cyclohexene + H_2	5	60	100	Cyclohexane (100)
Propionaldehyde[b] + H_2	30	100	100	n-Propanol (100)
Acetone + H_2	68	180	15	Propan-2-ol (100)
Crotonaldehyde + H_2	5	50	35	But-2-en-1-ol (15) Butyraldehyde (20) n-Butanol (65)
Crotonaldehyde + H_2[c]	1	50	10	But-2-en-1-ol (50) Butyraldehyde (50)
Hex-1-ene + CO–H_2	100	1440	30	n-Hexane (13) Hex-2-enes (23) C_7-Aldehydes (57) (70% linear) C_7-Alcohols (7)
Hex-1-ene + CO–H_2 (2:1)	100	1440	76	n-Hexane (5) Hex-2-enes (23) C_7-Aldehydes (67) (67% linear) C_7-Alcohols (5)
Hex-1-ene + CO–H_2 (3:1)	100	1440	24	n-Hexane (8) Hex-2-enes (22) C_7-Aldehydes (62) (69% linear) C_7-Alcohols (8)

[a] [Substrate]:[catalyst] = 100; products analysed by g.l.c. [b] [Substrate]:[catalyst] = 1000. [c] 100 °C.

$$OsHBr(CO)(PPh_3)_3$$

(**1**)

Hydroformylation of hex-1-ene is also catalysed by solutions of (**1**) in toluene at 150 °C and 100 atm of H_2–CO. Both the conversion and the selectivity for aldehydes increase on increasing the CO : H_2 ratio from 1 : 1 to 2 : 1; the use of higher proportions of CO results in a marked decrease of catalytic activity and little effect on the selectivity of the reaction. The amount of n-heptanal produced in all cases corresponds to *ca.* 70% of the aldehyde fraction. Table 1 shows the product distribution under various reaction conditions. Apart from a mention in the patent literature of an unspecified osmium salt complexed by phosphine ligands,[14] we believe this to be the first report of a hydroformylation reaction catalysed by a mononuclear osmium complex.

The catalyst is quantitatively recovered unchanged from all the low pressure reactions; under the hydroformylation conditions $OsH_2(CO)_2(PPh_3)_2$ is isolated at the end of the run (identified by i.r. spectroscopy) and mixtures of osmium complexes are obtained from the solutions after hydrogenation of propionaldehyde or acetone. Attempts to separate and characterise these mixtures are currently in progress but they can be re-used as recovered without any appreciable loss in catalytic activity. Furthermore, the versatile reactivity of this easily accessible complex may prove to be of use in organic syntheses.

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