Polyhedron Vol. 7, No. 14, pp. 1239–1242, 1988
Printed in Great Britain

0277–5387/88 $3.00+.00

HYDROGENATION OF ALKENES BY DIRUTHENIUM(II) TETRAACETATE

ALAN J. LINDSAY, GREGORY McDERMOTT and GEOFFREY WILKINSON*

Chemistry Department, Imperial College of Science and Technology, London SWY 2AY, U.K.

(*Received* 22 *January* 1988; *accepted* 9 *February* 1988)

Abstract—The metal–metal bonded carboxylates, $Ru_2(\mu\text{-}O_2CR)_4$, R = CH_3 and CF_3 have been studied as catalysts for the homogeneous hydrogenation of alk-1-enes. Evidence for interaction of H_2 with $Ru_2(O_2CMe)_4$ and of complex formation between alk-1-enes and the carboxylates has been obtained.

Both the ruthenium acetate compounds $Ru_2(O_2CCH_3)_4Cl$ and $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$ have been used as catalysts for the homogeneous hydrogenation of alkenes.[1,2] The former and its triphenylphosphine reaction product,[1] exhibit catalytic activity in the presence of strong, non-complexing acids and excess triphenylphosphine; in these cases the active system appears to involve cationic alkene–bis(triphenylphosphine)-ruthenium(II) species,[3] $[Ru(PPh_3)_2(alkene)]^{2+}$. The oxo-triruthenium cluster acts as a hydrogenation catalyst at elevated temperatures (> 80°C) in dimethylformamide, and mechanistic studies indicate that only one ruthenium centre of the ion $[Ru_3O(O_2CCH_3)_4(DMF)]^+$ is active in coordinating both the hydrogen and alkene molecules and in mediating the subsequent hydride transfer to the alkene.[2] Other catalytically active ruthenium complexes have been prepared[3] from the oxo-centred species but none retain the triruthenium centre.

All these ruthenium systems catalyse the reduction of terminal alkenes but have varying selectivities for the reduction of internal and cyclic alkenes. For example, protonated $Ru_2(O_2CCH_3)_4Cl$ solutions will not reduce cyclooctene whereas the oxo-centred cluster readily reduced cyclohexene. The extent of substrate isomerization during these reductions is usually less than 5%, which is in marked contrast to that observed for the system using rhodium acetate $Rh_2(O_2CCH_3)_4$.[4]

We now report the use of $Ru_2(O_2CCH_3)_4$[5] as a catalyst precursor for the homogeneous hydrogenation of alkenes and alkynes to alkanes. The complex is effective in methanol under ambient conditions and the reduction proceeds with no isomerization of the unsaturated substrate. Unlike the ruthenium acetate system noted earlier, $Ru_2(O_2CCH_3)_4$ does not require elevated temperatures or additional acid or phosphine ligands to induce catalytic activity.

RESULTS AND DISCUSSION

Methanolic solutions of $Ru_2(O_2CCH_3)_4$ hydrogenate terminal and cyclic monoenes, and terminal alkynes homogeneously at room temperature under 1 atm of hydrogen. Comparative rates given in Table 1 indicate the reactivity order, cyclic alkene > terminal alkene > terminal alkyne: hydrogenation occurs at similar rates in ethanol and in dimethylformamide but is markedly slower in CH_3CN and CH_2Cl_2 and does not occur in THF and benzene. No hydrogenation of internal monoenes, dienes or of other compounds such as ketones and imines was observed.

In the absence of alkene, diruthenium(II) tetraacetate takes up one molecule of hydrogen per dimeric unit. In the absence of hydrogen, there is evidently the formation of an alkene adduct with $Ru_2(O_2CCH_3)_4$. Thus the initial electronic absorption spectrum of $Ru_2(O_2CCH_3)_4$ in methanol (λ 445 nm, $\varepsilon = 880$ dm^3 mol^{-1} cm^{-1}) changes upon the addition of hydrogen or alkene to the solution as shown in Figs 1 and 2, respectively. NMR spectra of the reacting solutions of $Ru_2(O_2CCH_3)_4$ showed considerable line broadening indicating that the paramagnetism of the catalyst species was retained throughout. Upon completion of a hydrogenation

* Author to whom correspondence should be addressed.

Table 1. Representative hydrogenations using $[Ru_2(O_2CCH_3)_4]$[a]

Substrate	Time (min)[b]
Hex-1-ene	70
Oct-1-ene	85 (96)[c]
Cyclohexene	63
Cyclooctene	79 (300)[c]
Styrene	125
Hex-1-yne	570
Oct-1-ene	94[d]
Oct-1-ene	90[e]
Oct-1-ene	340[f]

[a] Reaction conditions: 50 cm^3 of 2 mM methanolic solution of complex, 25°C, 1 atm H_2, catalyst : substrate 1 : 15.

[b] Time for complete hydrogenation.

[c] Time for "complete" hydrogenation using $[Rh_2(O_2CCH_3)_4]$ under identical conditions.

[d,e,f] Solvent = ethanol, DMF, acetonitrile, respectively.

reaction the $Ru_2(O_2CCH_3)_4$ was easily recovered and could be reused without appreciable loss of activity.

No detailed mechanistic studies have been undertaken but the kinetics for the hydrogenation appear to be first-order in alkene at low alkene concentration for the solvents and substrates used; in all cases hydrogen consumption levelled off at an amount close to that required for complete hydrogenation of the unsaturated substrate. Analysis of the final solution by gas–liquid chromatography confirmed the complete conversion of the alkene or alkyne to alkane and the absence of any isomerization products. The absence of isomerization suggests that $Ru_2(O_2CCH_3)_4$ may be of more practical use than the rhodium analogue $Rh_2(O_2CCH_3)_4$, which leads to isomerization of

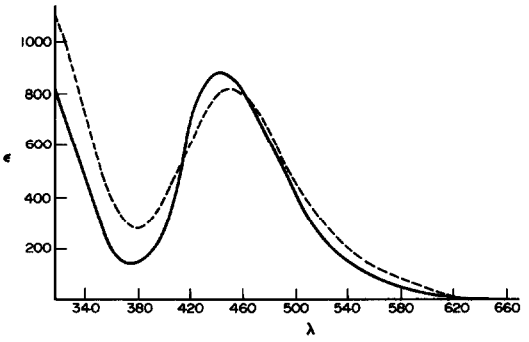


Fig. 1. Change in the electronic spectrum of $Ru_2(O_2CCH_3)_4$ in CH_3OH after stirring under hydrogen (1 h). Initial spectrum ——, hydrogenated spectrum – – –.

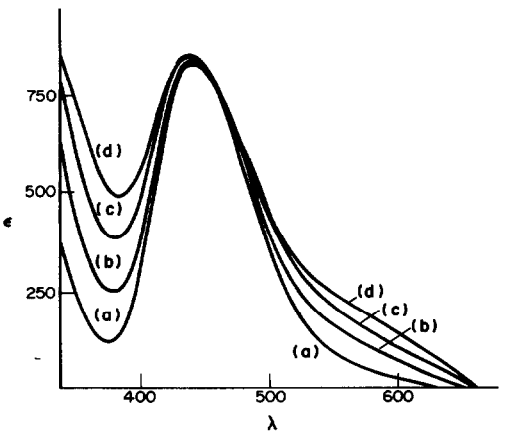


Fig. 2. Changes in the electronic spectrum on sequential addition of octene to $Ru_2(O_2CCH_3)_4$, 3 cm^3, 0.9 mM methanol solution at 25°C; (a) no octene; (b) 1.14 mM; (c) 2.4 mM; (d) 3.7 mM.

alk-1-enes.[4] The absorption of dihydrogen noted above suggests the formation of a hydride complex but the paramagnetism of the solutions and low solubilities prevented any characterization by IR and NMR spectra. Concentration of the hydride-containing solution under hydrogen results only in precipitation of the $Ru_2(O_2CCH_3)_4$. For the trioxoruthenium cluster[2] and rhodium(II) acetate[4] systems the initial activation step has been proposed to occur by hydrogenolysis for example:

$$Rh_2(O_2CCH_3)_4 + H_2 \rightleftharpoons HRh_2(O_2CCH_3)_3 + H^+ + {}^-O_2CCH_3. \quad (1)$$

Hydrogen uptake has also been observed for the oxo-centred triruthenium species and an inverse dependence of hydrogen uptake rate on free acetate concentration is observed;[2] a similar dependence has been observed for $Ru_2(O_2CCH_3)_4$ and the reaction with hydrogen is doubtless as in eq. (1). The requirement of a polar solvent (MeOH, DMF) for hydride formation suggests that solvation of the proton is necessary in addition to solvating the complex. In the hydrogenation cycle, we hence have the reactions (solvated methanol omitted):

$$Ru_2(O_2CMe)_4 + H_2 \rightleftharpoons HRu_2(O_2CMe)_3 + H^+ + MeCO_2^-$$

$$Ru_2(O_2CMe)_4 + \text{alkene} \rightleftharpoons Ru_2(O_2CMe)_4(\text{alkene})$$

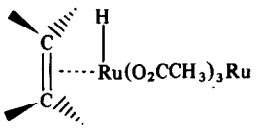
$$HRu_2(O_2CMe)_3 + \text{alkene} \rightleftharpoons Ru_2(O_2CMe)_3(\text{alkyl})$$

$$Ru_2(O_2CMe)_3(\text{alkyl}) + H^+ + MeCO_2^- \rightarrow Ru_2(O_2CMe)_4 + \text{alkane}.$$

There is no change in oxidation state of the ruthenium in any reaction and H-transfer to coor-

dinated alkene doubtless occurs at the same ruthenium atom.

In the second step it is assumed as usual that π-complex formation occurs between the alkene and the hydride species followed by an insertion of the coordinated alkene into the ruthenium–hydride bond to form an alkyl complex.[6] The most facile route for hydrogen transfer would be obtained when the alkene is π-bonded to the ruthenium–hydride centre as shown in **1**.



(1)

The absence of alk-1-ene isomerization indicates that the alkyl formation is irreversible unlike the analogous dirhodium(II) system where reversible alkyl formation results in significant isomerization.[4]

Although it might be expected on the basis of the above mechanism that the addition of a strong base, such as triethylamine, would favour hydrogenolysis and metal–hydride formation, the rate of hydrogenation is strongly inhibited by addition of triethylamine. Electronic spectra suggest that this results from the blocking of sites by axial coordination of the amine (L) through formation of an adduct of type $LRu_2(O_2CCH_3)_4L$, examples of which have been reported.[7]

Acidification of a methanolic solution of $Ru_2(O_2CCH_3)_4$ with an excess of a strong non-complexing acid such as HBF_4 produces a red colouration. The low catalytic activity of this red solution is however enhanced by the addition of triphenylphosphine and the yellow–brown solution so formed readily catalyses the hydrogenation of terminal and cyclic monoenes under hydrogen (cf. ref. 3); however, on standing, yellow $Ru(O_2CCH_3)_2(PPh_3)_2$ is deposited.

The complexing of the alkene noted above is not observed with $Rh_2(O_2CCH_3)_4$, but alkene complexing has been reported for the trifluoroacetate, $Rh_2(O_2CCF_3)_4$.[8] This adduct formation may be attributed to the electron deficient nature of the rhodium atoms in the trifluoroacetate complex compared to the acetate species. It is reasonable to assume that similar 1 : 1 adduct formation occurs in the ruthenium(II) system given the similarity in spectral shifts and the relatively electron deficient ruthenium centres in the tetraacetate. The absence of 2 : 1 complexes is probably due to the decreased acceptor capabilities of the 1 : 1 ruthenium adducts as observed for the rhodium(II) species.[9]

$Rh_2(O_2CCH_3)_4$ has been used as a catalyst for a variety of organic transformations including the autooxidation of alkenes[10] and the dehydrogenation of alcohols.[11] However, the air-sensitive nature of $Ru_2(O_2CCH_3)_4$ prevents its use as an autooxidation catalyst because of decomposition, while cleavage of the dimeric unit occurs with CO[7] thus preventing its use as a hydroformylation catalyst.

Hydrogenations using $Ru_2(O_2CCF_3)_4$

Qualitatively, we observe that the complex $Ru_2(O_2CCF_3)_4$ takes up hydrogen in the presence of terminal and cyclic monoenes on a significantly slower timescale than $Ru_2(O_2CCH_3)_4$. The times required for hydrogenation of alkenes, using the same conditions as for the $Ru_2(O_2CCH_3)_4$ experiments were about 18–24 h, regardless of whether a terminal or cyclic monoene was the substrate. The slowness of hydrogen uptake for the $Ru_2(O_2CCF_3)_4$ system is understandable in that the more electron-poor trifluoroacetato complex should be slower to add hydrogen than the corresponding acetato complex.

The electronic spectra of solutions following the addition of aliquots of alkene to a CH_2Cl_2 solution of $Ru_2(O_2CCF_3)_4$ show that the complex coordinates alkene, as judged by the change in the extinction coefficient (initially > 455 nm, ε 590 dm^3 mol^{-1} cm^{-1}) and slight shift in the λ_{max} for the absorption in the visible region similar to Fig. 2. A plot of $1/\Delta A$ vs 1/[alkene] provided evidence for a 1 : 2 complex between $Ru_2(O_2CCF_3)_4$ and alkene (L) presumably forming adducts of the type $LRu_2(O_2CCF_3)_4L$.

EXPERIMENTAL

Hydrated ruthenium "trichloride" was from Johnson Matthey plc. The carboxylates, $Ru_2(O_2CCH_3)_4$[5] and $Ru_2(O_2CCF_3)_4$[7] were prepared as before.[5] Solvents and substrates were rigorously purified and thoroughly degassed prior to use. Hydrogen was passed through an Englehard "Deoxo" catalyst before admission to the vacuum system.

Electronic spectra were recorded on a Perkin–Elmer 551 spectrophotometer. Successive injections of alkene into a 10^{-3} M solution of $Ru_2(O_2CCF_3)_4$ were made until the limiting λ_{max} of the complex could be determined. GLC analysis was carried out using a Perkin–Elmer Sigma 1B gas chromatographic system: for alkane and isomerized alkene detection a 4 m column of 15% Carbowax 20 M on Chromosorb (W.80–100 mesh) was used.

Hydrogen uptakes were measured using a mercury-filled gas burette and the thermostatted reaction flask was fitted with a Teflon stirrer rotating at the gas–liquid interface.

Acknowledgements—We thank Johnson Matthey plc for the loan of ruthenium and the SERC for support.

REFERENCES

1. P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick and G. Wilkinson, *J. Chem. Soc.* (*A*) 1970, 3322.
2. S. A. Fouda and G. L. Rempel, *Inorg. Chem.* 1979, **18**, 1.
3. R. W. Mitchell, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1973, 846.
4. B. C. Y. Hui, W. K. Teo and G. L. Rempel, *Inorg. Chem.* 1973, **12**, 758.
5. A. J. Lindsay, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1985, 2321.
6. P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc.* (*A*) 1968, 3143.
7. A. J. Lindsay, M. Motevalli, M. B. Hursthouse and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1987, 2723.
8. M. P. Doyle, S. N. Mahapatro, A. C. Carghey, M. S. Chinn, M. R. Colsman, N. K. Harn and A. N. Redwine, *Inorg. Chem.* 1987, **26**, 3070.
9. R. S. Drago, J. R. Long and R. Cosmano, *Inorg. Chem.* 1982, **21**, 2196.
10. A. F. Noels, A. J. Hubert and P. Teyssie, *J. Organomet. Chem.* 1979, **166**, 79.
11. S. Shimoda, T. Kojima and Y. Saito, *J. Mol. Catal.* 1983, **18**, 99.