ELSEVIER

Journal of Molecular Catalysis A: Chemical 96 (1995) 231–243

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Review

Homogeneous catalysis by osmium complexes. A review

Roberto A. Sánchez-Delgado [a,*], Merlin Rosales [b], Miguel A. Esteruelas [c], Luis A. Oro [c]

[a] *Chemistry Center, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

[b] *Inorganic Chemistry Laboratory, Facultad de Ciencias, La Universidad del Zulia (LUZ), Apartado 526, Maracaibo, Venezuela*

[c] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain*

Received 19 August 1994; accepted 1 September 1994

Abstract

Homogeneous catalysis by osmium complexes is more promising than hitherto realized. Most of the reactions studied have concentrated on simple model substrates, and therefore a demonstration of the utility of these catalysts for reactions of more sophisticated organic molecules is needed; highly selective reduction of terminal and internal carbon–carbon triple bonds in presence of other unsaturations within the same molecule should become an immediate goal. In view of the excellent results obtained in the asymmetric dihydroxylation of alkenes, other highly enantioselective processes, such as hydrogenation, oligomerization, hydrosilylation and hydroformylations may be envisaged with osmium complexes; catalytic activation of C–H, C–S, C–N, N–H, and OH bonds also seem reasonable and important targets. As a consequence of the high thermal and oxidative stability observed for osmium complexes, their syntheses, manipulation, and recycling may prove much simpler than for analogous, less robust catalysts derived from other metals, and these advantages may counter the higher cost involved in the case of osmium. Furthermore, this enhanced stability will certainly be convenient for kinetic and mechanistic studies which could lead to a deep understanding of the catalytic chemistry.

Keywords: Enantioselective processes; Homogeneous catalysis; Hydrogenation; Hydrosilylation; Hydroxylation; Osmium; Review; Thermal stability

1. Introduction

Homogeneous catalysis by platinum metal complexes has been traditionally dominated by ruthenium, rhodium and palladium [1]. The fact that 5d metals usually form more stable complexes than their 4d congeners has led to the general assumption that reactions typically conforming catalytic cycles, such as Lewis base addition–elimination, oxidative addition–reductive elimination, insertion–deinsertion, etc., are too slow for third row metal complexes to be of any practical application in catalysis. A judicious choice of the metal–ligand system, however, may lead to highly efficient catalysts, as demonstrated by platinum hydroformylation [2], and by the rich catalytic chemistry of iridium complexes developed recently [3,4]. In the past few years, a number of interesting examples of organic transformations catalyzed by osmium complexes have emerged in the literature, indicating that this still relatively undeveloped field offers considerable catalytic

* Corresponding author.

SSDI 1381-1169(94)00039-5

potential to be exploited in the near future. Here we provide an account of the published work concerning the use of osmium complexes in homogeneous catalytic reactions, in the hope of stimulating further research in this area.

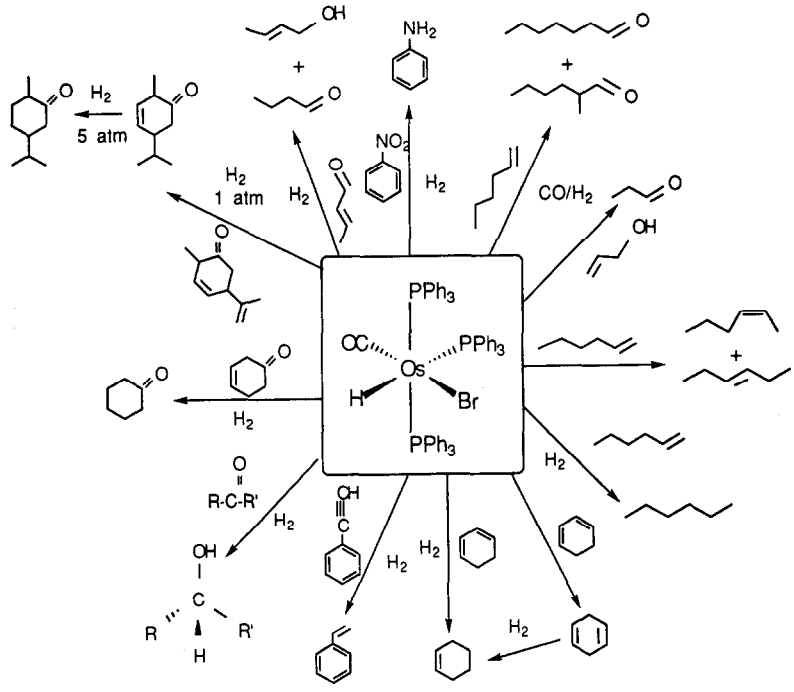
2. Mononuclear complexes

For mononuclear complexes, the earliest reports on catalytic activity are some brief mentions by Vaska [5] and Mitchell [6] on the ability of $OsHCl(CO)(PPh_3)_3$ to hydrogenate C=C bonds. Chatt and coworkers also described some experiments on the isomerization and hydrogenation of octenes catalyzed by $OsH_2(PEtPh_2)_4$, $OsH_2(CO)(PEtPh_2)_3$, and $OsH_4(PEtPh_2)_3$ [7]. Robinson and coworkers have described the catalytic dehydrogenation of alcohols, as well as the isomerization and transfer hydrogenation of acetylenes by ruthenium and osmium trifluoroacetate complexes [8]; in these papers, however, it is only stated that osmium complexes are less effective than their ruthenium analogs, but the catalytic data presented concern exclusively the latter. Olefin hydrogenation by use of $OsHCl(CO)(PPh_3)_3$, $OsH_3(PPh_3)_3$ and $OsHCl_2(AsPh_3)_3$ [9], as well as hydroformylation by mixtures of osmium salts with phosphines [10] have been claimed in the patent literature.

The full potential of hydrido-phosphine osmium complexes as efficient and versatile catalysts for organic reactions has only recently begun to be exploited in some laboratories, including ours in the case of compounds of the type $OsHX(CO)(PR_3)_{2,3}$ and related species.

2.1. *The complex $OsHBr(CO)(PPh_3)_3$*

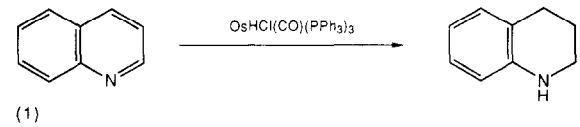
The complex $OsHBr(CO)(PPh_3)_3$, first synthesized by Vaska in 1961 [11] by prolonged reaction of $[OsBr_6]^{2-}$ with PPh_3 in boiling 2-methoxyethanol, combines good solubility in a number of common solvents with high thermal and oxidative stability. The structure of this compound [12], together with a summary of its versatile catalytic chemistry developed in our laboratories [13–16] are shown in Scheme 1.



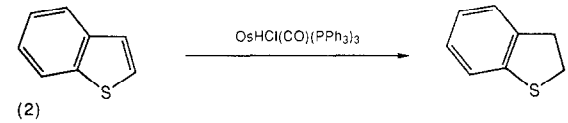
Scheme 1.

Isomerization reactions are conducted at 100°C and include double bond migration and *cis–trans* isomerization, isomerization of cyclohexa-1,3-diene to cyclohexa-1,4-diene, and of allyl alcohol to propionaldehyde. Hydrogenation of terminal as well as internal olefins, dienes, and acetylenes is also achieved at 100°C and 1 atm H_2. The most remarkable reactions are the highly selective reductions of dienes to monoenes, and of alkynes to alkenes. The C=O bonds in aldehydes and ketones are also efficiently hydrogenated by $OsHBr(CO)(PPh_3)_3$. Crotonaldehyde reduction by this complex produces a 1:1 mixture of the unsaturated alcohol and the saturated aldehyde, while the fully hydrogenated product is not formed. Cyclohex-2-en-1-one, on the other hand, undergoes exclusive C=C bond reduction under 1 atm H_2 or, more rapidly, in boiling isopropanol under N_2. In the case of L-carvone, the exocyclic C=C bond is specifically hydrogenated by $OsHBr(CO)(PPh_3)_3$ under 1 atm H_2; by raising the H_2 pressure to 5 atm, both C=C bonds are reduced. Pressures of the order of 60 atm result in the formation of the corresponding saturated alcohol.

Nitrobenzenes are also selectively reduced by $OsHBr(CO)(PPh_3)_3$ to the corresponding anilines under hydrogen, syngas and water–gas shift conditions; the highest rates were observed under CO/H_2O in alkaline medium [16]. Finally, olefin hydroformylation is catalyzed by $OsHBr(CO)(PPh_3)_3$ at 150°C and 100 atm CO/H_2, reaching maximum rates of ca. 3 turnovers h^{-1} with selectivities of 67% for aldehydes (n/i ratio ca. 2) [13,14]. Also, the closely related compound $OsHCl(CO)(PPh_3)_3$ showed to be a very efficient catalyst precursor for the specific homogeneous hydrogenation of the heterocyclic ring in quinoline and benzothiophene (Eqs. 1 and 2). Reduction of the sulfur heterocycle required more drastic conditions than that of the nitrogen-containing ring. Decomposition of the complex is not apparent in the time range investigated; however, prolonged reaction in the hydrogenation of benzothiophene did lead to some decomposition and a consequent loss in catalytic activity [17].



(1)



(2)

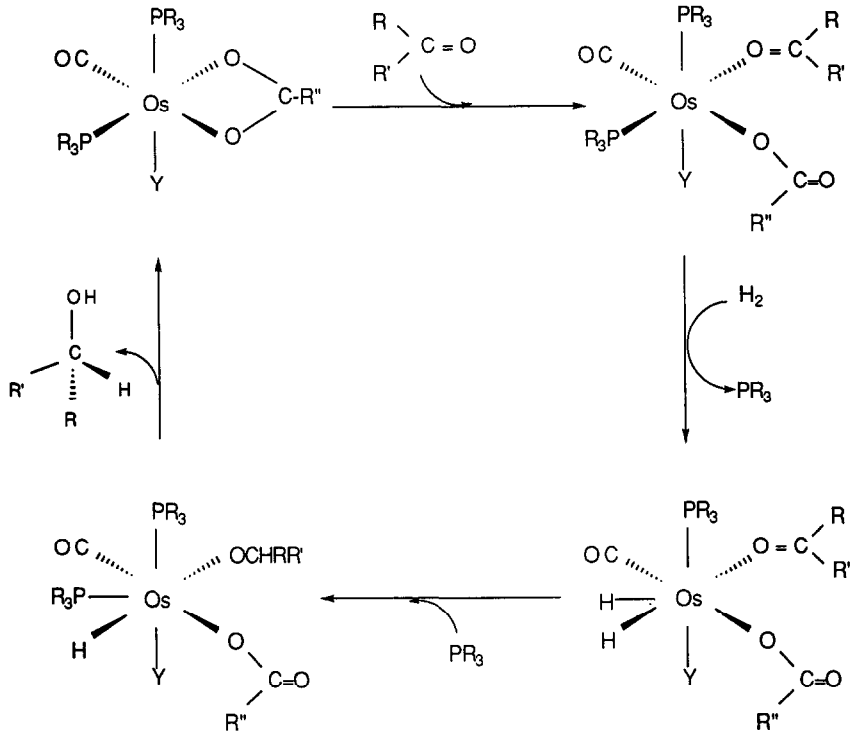
2.2. Carboxylate complexes

The triphenylphosphine complexes $OsHX(CO)(PPh_3)_3$ (X = Cl, Br) react with acetic acid to yield the corresponding carboxylate derivatives $OsX(OCOCH_3)(CO)(PPh_3)_2$, characterized spectroscopically and crystallographically for X = Br [18]. These complexes have proved to be very active in the hydrogenation of the C=O bonds of aldehydes (140°C, 30 atm H_2) and ketones (140°C, 60 atm H_2). The reaction mechanism illustrated in Scheme 2 involves a bidentate–monodentate equilibrium for the carboxylate ligand, through which coordinative unsaturation and, consequently, catalytic activity is attained [19].

Carboxylate complexes of formula $OsH(\eta^2\text{-}O_2CR^*)(CO)(P^iPr_3)_2$ (R^* = (*S*)-CH (Naph-OMe)Me, (*R*)-CH(OMe)Ph, (*R*)- C(CF_3)-(OMe)Ph, (*S*)-CHOC(=O)CH_2CH_2) have been found to be active catalysts for the asymmetric hydrogen transfer reaction from 2-propanol to acetophenone [20].

2.3. Arsine complexes

As an extension of the work on osmium PPh_3 complexes, the synthesis and characterization of analogous arsine complexes $OsHCl(CO)(AsPh_3)_3$, $OsHCl(CO)(AsPh_3)$ (arphos) and $OsCl(CO)(OCOCH_3)(AsPh_3)_2$ were also reported. These new osmium arsine complexes



Scheme 2.

were also efficient precatalysts for the homogeneous hydrogenation of propionaldehyde under moderate reaction conditions [21].

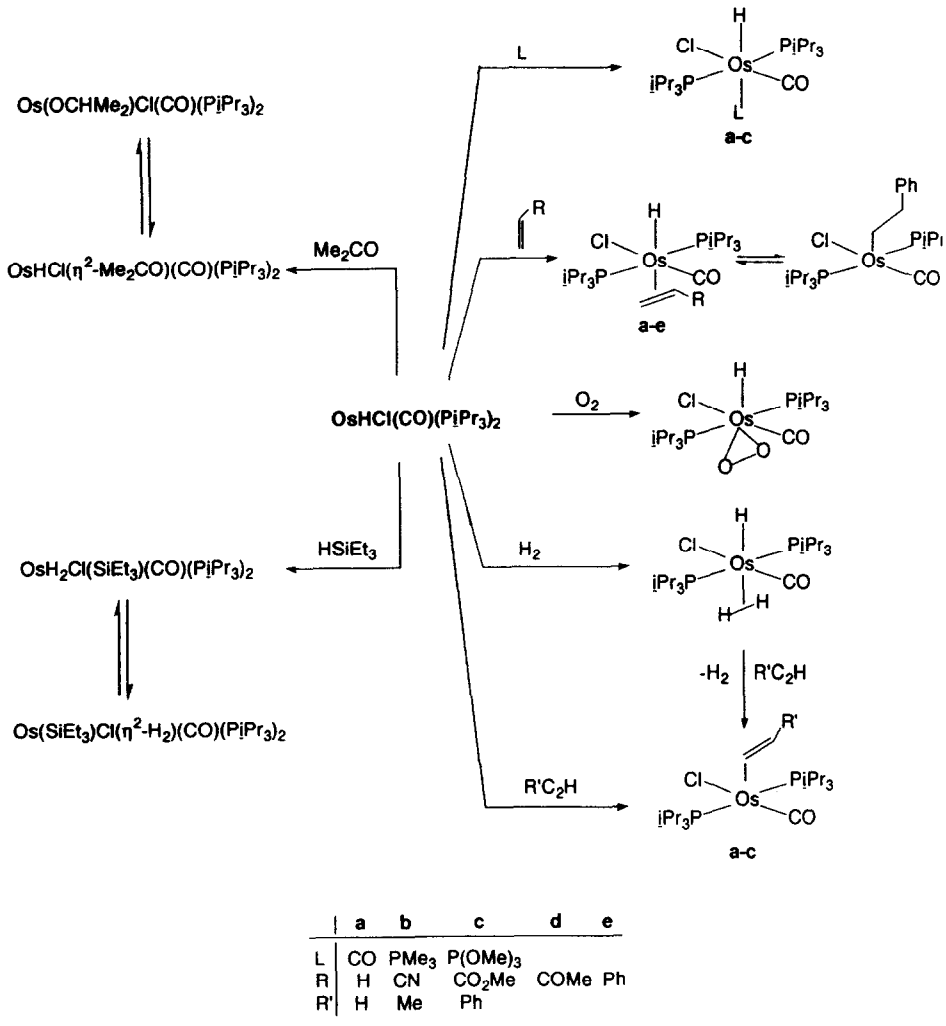
2.4. *The complexes $OsHCl(CO)(PR_3)_2$: the Zaragoza–Würzburg catalysts*

These complexes where PR_3 is a bulky trialkylphosphine (P^iPr_3, PMe^tBu_2) have been prepared by reaction of $OsCl_3 \cdot H_2O$ with the appropriate phosphorus ligand in boiling methanol. Spectroscopic data indicate a square base pyramidal geometry, with the hydride occupying the apical position and the phosphines disposed in a *trans* arrangement [22,23].

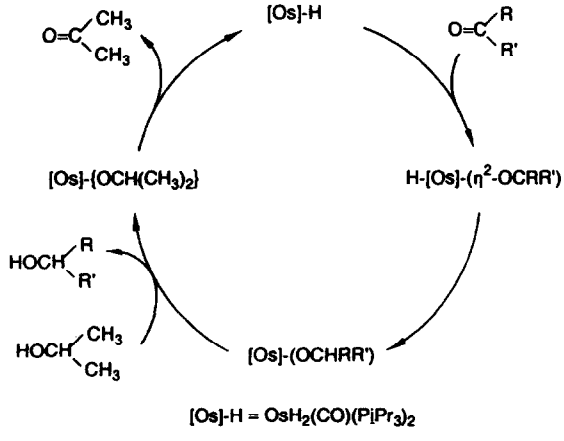
At room temperature, the complex $OsHCl(CO)(P^iPr_3)_2$ adds Lewis bases that are not bulky (e.g. CO, PMe_3 and $P(OMe)_3$) to form octahedral compounds of formula $OsHCl(CO)L(P^iPr_3)_2$ [22]. Oxygen, hydrogen, and olefins such as ethylene, methyl acrylate, acrylonitrile and methyl vinyl ketone are also coordinated [22,24]. Upon reaction with $HSiEt_3$, the dihydrogen complex $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ is formed [25]. Alkynes, styrene and acetone undergo insertion into the Os–H bond [26–28] (Scheme 3).

Catalytic reactions with these compounds include hydrogen transfer from 2-propanol to cyclohexanone, acetophenone [29], benzylideneacetone, benzylideneacetophenone [30] and phenylacetylene [31], hydrogenation with molecular hydrogen of styrene, cyclohexene, cyclohexadienes, phenylacetylene, diphenylacetylene and benzylideneacetone [24] and hydrosilylation of phenylacetylene [25].

The hydrogen transfer reactions are usually performed in boiling 2-propanol under N_2 or Ar and in the presence of $NaBH_4$. Under catalytic conditions the complex $OsHCl(CO)(P^iPr_3)_2$ reacts with $NaBH_4$ to give initially $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ [23]. Under reflux in 2-propanol it decomposes to the tetrahydrido $OsH_4(CO)(P^iPr_3)_2$ [32], which affords $OsH_2(CO)(P^iPr_3)_2$ that acts as the catalyst of the reactions. Kinetic and spectroscopic studies car-



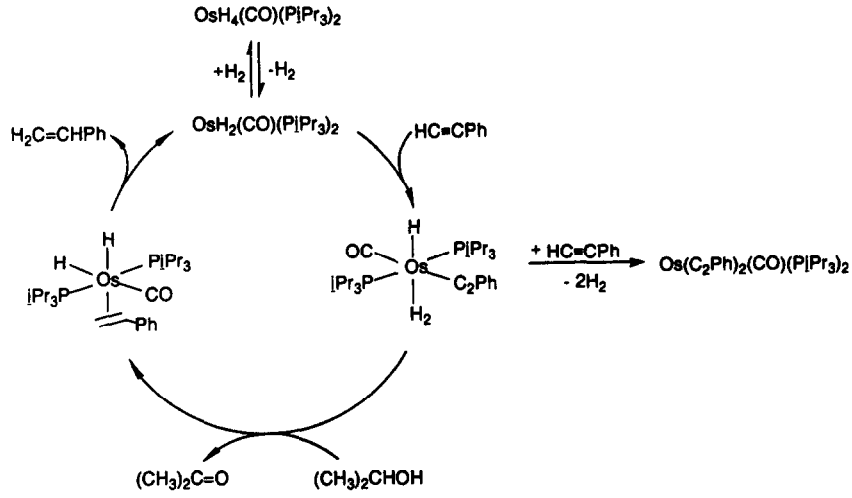
Scheme 3.



Scheme 4.

ried out on the hydrogen transfer reaction from 2-propanol to cyclohexanone suggests that these reactions involve four steps (Scheme 4) [28]: (i) coordination of the ketone to the coordinatively unsaturated dihydride $OsH_2(CO)(P^iPr_3)_2$, (ii) formation of an alkoxy metal intermediate by hydrogen migration from the metal to the ketonic double bond, (iii) exchange of the alkoxy group by reaction with the alcohol, which acts as solvent, and (iv) a β-elimination process.

Competitive reactions (ketone–olefin) indicate that ketones are reduced preferentially to olefins; however, α,β-unsaturated ketones are selectively reduced to the corresponding saturated ketones.



Scheme 5.

At long reaction times saturated alcohols may be obtained [30].

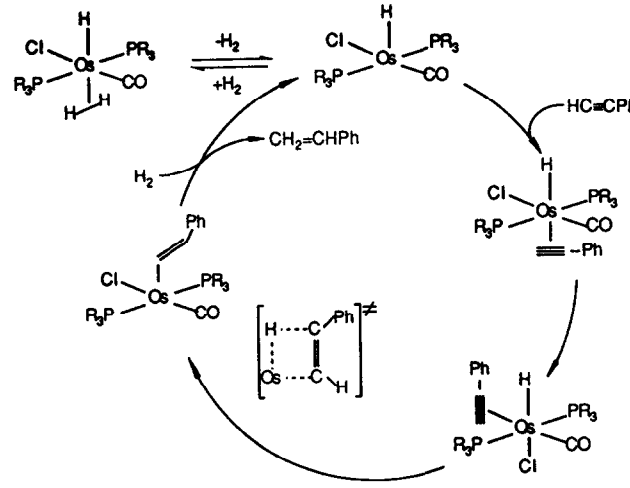
A detailed study of the reaction rate of the reduction of phenylacetylene by hydrogen transfer from 2-propanol has shown that, initially, the solution which contains $OsH_4(CO)(P^iPr_3)_2$ rapidly reduces the substrate to styrene. However, the reaction rate falls, progressively, as the colorless solution of $OsH_4(CO)(P^iPr_3)_2$ is transformed into a dark red solution of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ [31]. Spectroscopic investigations have shown that the tetrahydrido complex $OsH_4(CO)(P^iPr_3)_2$ reacts with the stoichiometric amount of phenylacetylene to give molecular hydrogen and the alkynyl-dihydrogen derivative $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, which reacts with a second molecule of phenylacetylene to give $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ and molecular hydrogen. Under argon atmosphere, the stirring of a solution of $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, in 2-propanol leads to $OsH_2(\eta^2\text{-}CH_2{=}CHPh)(CO)(P^iPr_3)_2$ and acetone in quantitative yield. These observations have been elegantly accommodated by the cycle shown in Scheme 5, which contains the stoichiometric steps that could summarize the process of hydrogen transfer from 2-propanol to phenylacetylene [33].

Under molecular hydrogen, dienes are reduced to mixtures of the monoene and the alkane with moderate to good selectivities for the monoolefin. Alkynes and α,β-unsaturated ketones, on the other hand, are selectively hydrogenated to the corresponding olefins and saturated ketones [24].

The kinetics and the mechanisms of the hydrogenation of phenylacetylene to styrene [27] and benzylideneacetone to 4-phenylbutan-2-one [34] catalyzed by $OsHCl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, PMe^tBu_2) have been investigated in detail. For the reduction of the alkyne, with both catalysts the rate law is

$$-\frac{d[\text{phenylacetylene}]}{dt} = k[\text{phenylacetylene}][\text{Os}]P_{H_2}$$

Scheme 6 illustrates the catalytic cycle for the selective phenylacetylene hydrogenation. The reaction of the monohydrides with the alkyne is rapid and leads to stable 16-electron vinyl complexes $Os((E)\text{-}CH{=}CHPh)Cl(CO)(PR_3)_2$. The elementary steps involved in the transformation of the styryl derivatives are too rapid to be observed by spectroscopic methods. However, it has been shown by NMR spectroscopy that acetylenedicarboxylic methyl ester coordinates to $OsHCl(CO)(P^iPr_3)_2$ *trans* to the hydride at room temperature; then rearrangement to the *cis* isomer takes place, followed by insertion to yield the corresponding vinyl species. The slow step of this

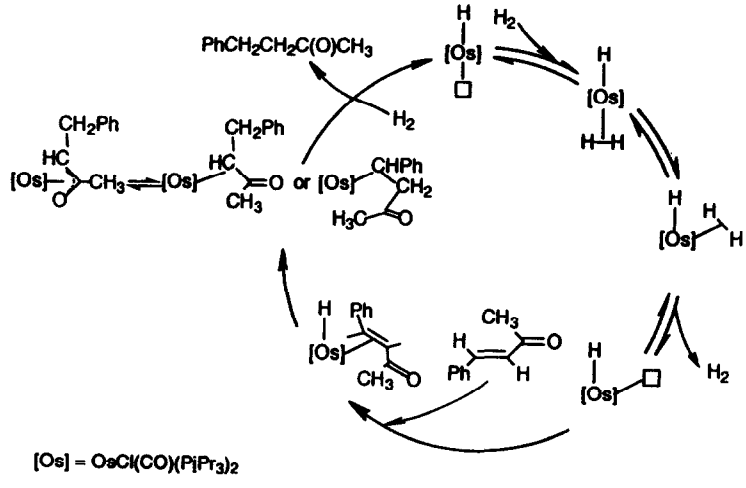


Scheme 6.

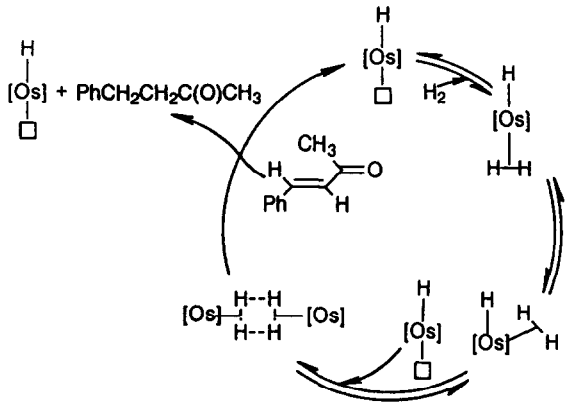
catalytic cycle is the reaction of the five-coordinate complexes with hydrogen to yield the olefin and regenerate the catalysts.

The high selectivity observed for the hydrogenation of phenylacetylene to styrene seems to be thermodynamically controlled. The independent study of the reduction of the C≡C and C=C bonds indicates that the latter is kinetically favored. However, the vinyl complexes are the main species under catalytic conditions. These derivatives represent thermodynamic sinks that cause virtually all the osmium present in solution to be tied up in this form, and consequently, the kinetically unfavorable pathway becomes the only one available in the presence of phenylacetylene.

The mechanisms deduced for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one, on the basis of kinetic results and spectroscopic observations (Schemes 7 and 8), illustrate some roles of the dihydrogen complexes in catalysis. The complex $OsHCl(CO)(P^iPr_3)_2$, initially inactive is activated as a result of the formation of *trans-(hydrido, dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, which isomerizes to *cis-(hydrido, dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ and subsequently dissociates



Scheme 7.



Scheme 8.

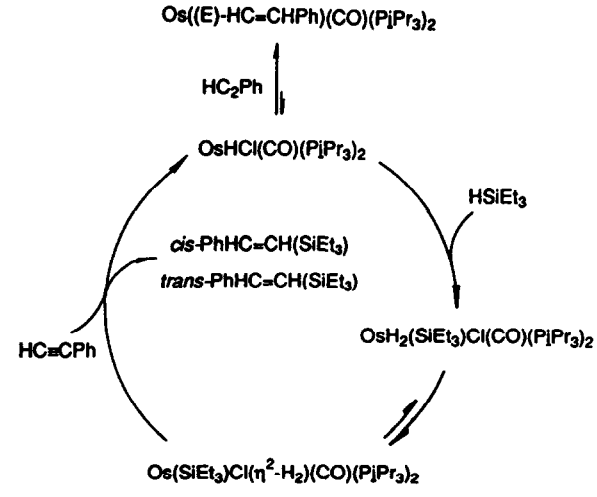
the η^2-H_2 ligand (Scheme 7). Under catalytic conditions, the complex $OsHCl(CO)(PMe^tBu_2)_2$ is in a dynamic equilibrium with *trans*-(*hydrido, dihydrogen*)-$OsHCl(\eta^2\text{-}H_2)(CO)(PMe^tBu_2)_2$, which also isomerizes to *cis*-(*hydrido, dihydrogen*)-$OsHCl(\eta^2\text{-}H_2)(CO)(PMe^tBu_2)_2$. The subsequent reaction of this derivative with $OsHCl(CO)(PMe^tBu_2)_2$ leads to a binuclear intermediate, which by reaction with benzylideneacetone gives the saturated ketone and regenerates the catalyst (Scheme 8). It has been proposed that the binuclear intermediate could be *trans*-$[OsCl(CO)(PMe^tBu_2)_2]_2H_4$, containing a planar tetragon of cyclically bound hydrogen atoms [34].

trans- and *cis*-$PhCH{=}CH(SiEt_3)$ are selectively obtained in high yield, by reaction of phenylacetylene with triethylsilane in the presence of $OsHCl(CO)(P^iPr_3)_2$. Although the vinyl compound $Os((E)\text{-}CH{=}CHPh)Cl(CO)(P^iPr_3)_2$ is the main species under hydrosilylation conditions, the catalytic reaction proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (Scheme 9) [25].

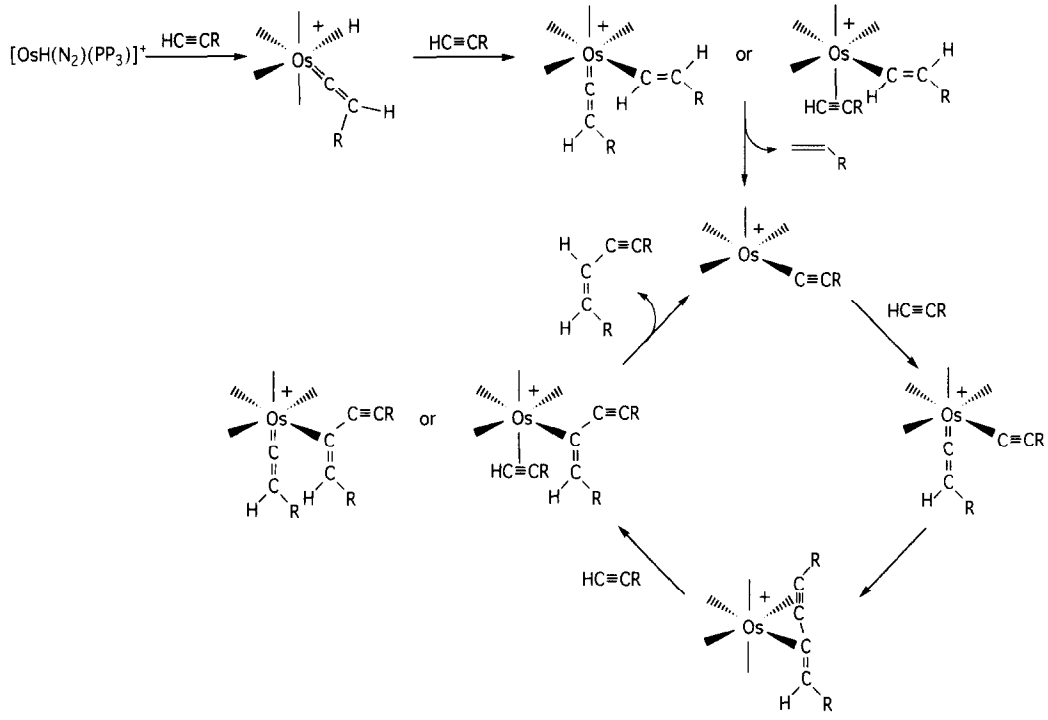
2.5. The complex $OsH_2Cl_2(P^iPr_3)_2$

Under hydrogen atmosphere, solutions of this compound in 2-propanol, 1,2-dichloroethane or toluene catalyze the hydrogenation of styrene, methylstyrene, cyclohexene and cyclooctene at considerable initial rates, which depend both on the solvent and the alkene substrate [35]. $OsH_2Cl_2(P^iPr_3)_2$ also catalyzes the hydrogenation of the C=C bond of α,β-unsaturated ketones as well as dienes. 1,5-Cyclooctadiene is more rapidly reduced than the 1,3-isomer. This finding is also true in a competitive sense: 1,3-cyclooctadiene is not hydrogenated until the concentration of the 1,5-isomer is almost zero. The selectivity for these reactions to give cyclooctene is poor.

Ketones such as cyclohexanone, methylcyclohexanone, and acetophenone are not hydrogenated under atmospheric pressure of hydrogen. Also under hydrogen transfer conditions (boiling 2-propanol under Ar), the catalytic activity of the dichloro dihydrido compound is rather poor; after 3 h the conversion to the corresponding alcohol is not more than 4%. The addition of $NaBH_4$, however, gives rise to a significant increase in activity [35]. Under these conditions, the complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with $NaBH_4$ to give initially $OsH_3(\eta^2\text{-}H_2BH_2)(P^iPr_3)_2$, which decomposes to $OsH_6(P^iPr_3)_2$ [36]. As this hexahydrido is coordinatively saturated, its activation most probably involves the loss of one dihydrogen molecule per molecule of $OsH_6(P^iPr_3)_2$ to produce $OsH_4(P^iPr_3)_2$, which presumably acts as the active catalyst [35].



Scheme 9.



Scheme 10.

The reaction of the complex $OsH_2Cl_2(P^iPr_3)_2$ with $K(CH_3CO_2)$ in methanol affords the trihydride $OsH_3(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2$. This complex reacts with phenylacetylene to give the hydridovinylidene complex $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(P^iPr_3)_2$ which catalyzes the dimerization of phenylacetylene to give a mixture of *trans*-PhC≡CCH=CHPh and *cis*-PhC≡CCH=CHPh in a 2:5 molar ratio [37].

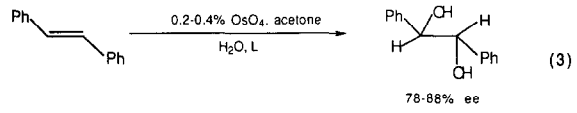
2.6. The complexes $[OsH(L)(PP_3)]BPh_4$

Bianchini et al. have recently observed that complexes of the type $[OsH(L)(PP_3)]BPh_4$, where $L = H_2$, N_2 and $PP_3 = P(CH_2CH_2PPh_2)_3$, are efficient catalyst precursors for the reduction of α,β-unsaturated ketones and for the regio- and stereoselective dimerization of acetylenes [38]. Thus, hydrogen-transfer reaction of α,β-unsaturated ketones catalyzed by $OsH(H_2)(PP_3)]BPh_4$ must be performed in propan-2-ol and cyclopentanol and its selectivities depend on the structure of the substrate; α,β-unsaturated ketones are reduced to saturated ketones via isomerization of the initially produced allylic alcohols [38a]. Complex $[OsH(N_2)(PP_3)]BPh_4$ catalyzes the dimerization of terminal alkynes to disubstituted but-3-en-1-ynes. Interestingly, at 0°C, this compound reacts with the stoichiometric amount of (trimethylsilyl)acetylene to give a mixture of the cationic compounds $[(PP_3)OsH(C{=}CHSiMe_3)]BPh_4$ and (*E*)-$[(PP_3)Os\{\eta^3\text{-}(SiMe_3)C_3{=}CH(SiMe_3)\}]$-$BPh_4$. A detailed study of this reaction under different experimental conditions together with the detection of some intermediates led to the mechanism shown in Scheme 10 [38b].

2.7. Osmium catalyzed asymmetric olefin dihydroxylation

A novel catalytic process based on the enantioselective addition of OsO_4 to olefins and dienes to

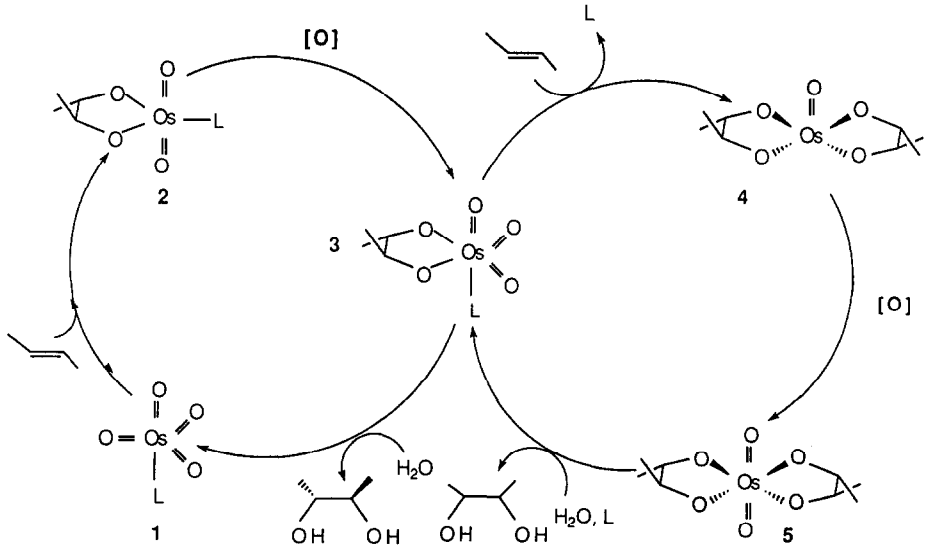
produce vicinal diols has recently been described by Sharpless and coworkers [39–42]. The simplicity and effectiveness of this procedure is illustrated by the reaction of (*E*)-stilbene, which is completely digested to a homogeneous solution of the diol product when a suspension of the olefin in acetone–water is allowed to stand overnight in the refrigerator with OsO_4 in presence of the cinchona alkaloid derivatives dihydroquinine or dihydroquinidine as chiral ligands (Eq. 3):



(3)

The reaction is of general application to a number of olefins, producing the diols with yields of 80–95% and enantiomeric excesses (ee) of 33–88% [39].

Mechanistic insight into this reaction led to a greatly improved process by the trivial modification of adding the olefin slowly to the catalytic mixture. All the alkenes studied gave higher ee's and reacted faster than in the original method. This and other observations were explained by a mechanism involving two distinct catalytic cycles operating for the conversion of the olefin to the vicinal diol. As shown in Scheme 11, OsO_4 adds one molecule of the chiral ligand to produce the isolated intermediate OsO_4L (**1**), which in turns reacts with the olefin to yield the dioxomonoglycolate species **2** (also isolated). Oxidation of the latter yields a putative Os(VIII) trioxomonoglycolate complex **3** which is a key intermediate occupying the pivotal position at the junction between the two cycles. The properties of this intermediate are believed to determine how the diol production is partitioned between the cycles which is crucial in determining high ee. If complex **3** is allowed to be hydrolyzed in the absence of excess alkene, then **1** is regenerated, and the maximum ee is achieved as determined during the addition of **1** to the olefin. When excess alkene is present in the reaction medium, an alternative reaction with a second molecule of olefin becomes important, yielding the oxodiglycolate intermediate **4** (isolated), which is then oxidized to the dioxodiglycolate **5** and subsequently hydrolyzed to produce the diol and regenerate **3**. Turning on this second cycle, which implies displacement of the chiral ligand from the osmium center, results in lower ee's, and in reduced turnover frequencies [40]. In later work, the reaction was further modified by the use of phthalazine as the chiral ligand, which produces ee's in excess of 90% [41]. Also,



Scheme 11.

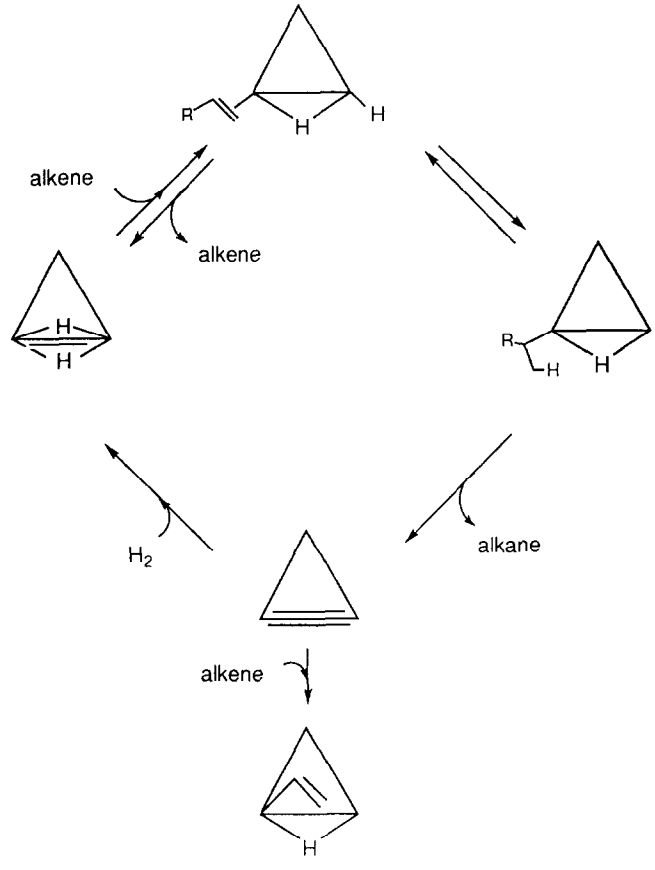
the reaction has been applied to conjugated and non-conjugated dienes using $K_3Fe(CN)_6$ as the stoichiometric oxidant and phthalazine as the ligand [42].

3. Cluster compounds

The use of osmium carbonyl clusters as catalyst precursors for a variety of organic reactions has been the subject of a number of papers. The trinuclear cluster $Os_3(CO)_{12}$ is an efficient precatalyst for alkene isomerization [43], alkyne cyclotrimerization [44], C–N bond activation [45], hydroformylation [46], and water–gas shift [46,47] and CO hydrogenation [48] reactions in solution.

The mechanisms of these and other 'cluster-catalyzed' reactions have not generally been well established. In particular, the question of whether the cluster itself is the species responsible for the catalysis has been the subject of much debate, and remains largely unsolved. The mere fact that the cluster is recovered intact from the catalytic runs, or in some cases, is the only species observed under catalytic conditions by IR or NMR spectroscopy, must be interpreted with caution. It is sufficient to transform a small amount of the cluster – not recoverable or even observable – into a very reactive mononuclear fragment, to obtain a highly active catalytic solution.

Some detailed mechanistic studies have addressed this problem in the case of osmium compounds. The unsaturated dihydrido derivative $Os_3H_2(CO)_{10}$ has been reported by Shapley to hydrogenate olefins in solution [49]. Through a combination of chemical and spectroscopic methods it was possible to establish the catalytic cycle



Scheme 12.

shown in Scheme 12, implicating only trinuclear species throughout the hydrogenation process. Similarly, the closely related silica-supported cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)$ was found by Basset and coworkers [50] to be an efficient catalyst for the hydrogenation of ethylene under mild conditions; kinetic, as well as volumetric and IR studies on this system and on a soluble $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ analogue led to a proposed mechanism involving the intact triosmium framework in all the elementary steps conforming the catalytic cycle; a facile $3e \leftrightarrow 1e$ interconversion of surface-oxygen ligands was said to provide the appropriate energy balance for cluster catalysis without fragmentation. Another system which appears to hydrogenate olefins through a cycle involving only trinuclear species is the $[Os_3(NCO)(CO)_{11}]^-$ anion reported by Gladfelter [51]; in this case the $\mu\text{-}\eta^2 \leftrightarrow \eta^1$ transformation of the isocyanate ligand provides the vacant coordination site required for the catalysis to proceed, without the need to break any Os–Os bonds.

Sánchez-Delgado and coworkers reported that a number of other tri- and tetranuclear osmium clusters can serve as catalyst precursors for C=C bond hydrogenation under moderate reaction conditions; the fact that some structure–activity relationships could be established led to the idea that the intact clusters could be the actual catalytic species [52]. However, more detailed work by this group on the kinetics of styrene hydrogenation with neutral and anionic tetrahedral and 'butterfly' shaped tetraosmium clusters concluded that fragmentation of these clusters yielding low concentrations of highly active species of lower nuclearity was the rule whenever important catalytic activity was observed [53].

4. Future prospects

It is clear from the examples presented above that homogeneous catalysis by osmium complexes is more promising than hitherto realized. Most of the reactions studied so far have concentrated on simple model substrates, and therefore a demonstration of the utility of these catalysts for reactions of more sophisticated organic molecules is needed; highly selective reduction of terminal and internal carbon–carbon triple bonds in presence of other unsaturations within the same molecule should be an immediate goal. In view of the excellent results obtained in the asymmetric dihydroxylation of alkenes, other highly enantioselective processes, such as hydrogenation, oligomerization, hydrosilylation and hydroformylations may be envisaged with osmium complexes; catalytic activation of C–H, C–S, C–N, N–H, and OH bonds seem also reasonable and important targets.

As a consequence of the high thermal and oxidative stability observed for osmium complexes, their syntheses, manipulation, and recycling may prove much simpler than for analogous, less robust catalysts derived from other metals, and these advantages may counter the higher cost involved in the case of osmium. Furthermore, this enhanced stability will certainly be convenient for kinetic and mechanistic studies which may lead to a deep understanding of the catalytic chemistry.

In conclusion, a much greater interest in this largely unexplored area of chemistry is to be expected in the near future.

Acknowledgements

We thank the DGICYT (Project PB92-0092, Programa de Promoción General del Conocimiento) and EU (Project 'Selective Processes and Catalysis involving Small Molecules').

References

[1] G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vols. 4, 5, 6, 8, Pergamon, Oxford, 1982.

[2] (a) L. Markó, Proc. Chem. Soc. (London), (1962) 67; (b) C. Hsu and M. Orchin, J. Am. Chem. Soc., 97 (1975) 3553 (c) I. Schwager and J.F. Knifton, J. Catal., 45 (1976) 256.

[3] (a) R.H. Crabtree, Acc. Chem. Res., 12 (1979) 331; R.H. Crabtree, J.M. Mihelcic and J.M. Quirk, J. Am. Chem. Soc., 101 (1979) 7738; (c) R.H. Crabtree, J.M. Mihelcic and J.M. Quirk, J. Am. Chem. Soc., 104 (1982) 107; (d) A.S. Goldman and J. Halpern, J. Am. Chem. Soc., 107 (1987) 7537.
[4] (a) L.A. Oro, J.A. Cabeza, C. Cativiela, M.D. Díaz de Villegas and E. Meléndez, J. Chem. Soc., Chem. Commun., (1983) 1383; (b) L.A. Oro, M.J. Fernández, M.A. Esteruelas and M.S. Jiménez, J. Mol. Catal., 37 (1986) 151; (c) M.J. Fernández, M.A. Esteruelas, M. Covarrubias and L.A. Oro, J. Organomet. Chem., 316 (1986) 343; (d) M.J. Fernández, M.A. Esteruelas, M.S. Jiménez and L.A. Oro, Organometallics, 5 (1986) 1519.
[5] L. Vaska, Inorg. Nucl. Chem. Lett., 1 (1965) 89.
[6] T.R.B. Mitchell, J. Chem. Soc. (B), (1970) 823.
[7] B. Bell, J. Chatt and G.J. High, J. Chem. Soc., Dalton Trans., (1977) 997.
[8] (a) A. Dobson and S.D. Robinson, Inorg. Chem., 16 (1977) 137; (b) A. Dobson, D.S. Moore, S.D. Robinson, M.B. Hursthouse and L. New, Polyhedron, 4 (1985) 1119.
[9] P. Fotis and J.D. McCollum, US Pat. 3 324 018 (1967).
[10] L. Slaugh and R.D. Mullineaux, US Pat. 3 239 571 (1966).
[11] L. Vaska, J. Am. Chem. Soc., 86 (1964) 1943.
[12] P.L. Orioli and L. Vaska, Proc. Chem. Soc. London, (1962) 333.
[13] R.A. Sánchez-Delgado, A. Andriollo and N. Valencia, J. Chem. Soc., Chem. Commun., (1983) 44.
[14] R.A. Sánchez-Delgado, A. Andriollo, E. González, N. Valencia, J. Espidel and V. León, J. Chem. Soc., Dalton Trans., (1985) 1859.
[15] R.A. Sánchez-Delgado, A. Andriollo and N. Valencia, J. Mol. Catal., 24 (1984) 217.
[16] R.A. Sánchez-Delgado and B.A. Oramas, J. Mol. Catal., 36 (1986) 283.
[17] R.A. Sánchez-Delgado and E. González, Polyhedron, 8 (1989) 1431.
[18] R.A. Sánchez-Delgado, U. Thewalt, N. Valencia, A. Andriollo, R.L. Márquez-Silva, J. Puga, H. Schöllhorn, H.P. Klein and B. Fontal, Inorg. Chem., 25 (1986) 1097.
[19] R.A. Sánchez-Delgado, N. Valencia, R.L. Márquez-Silva, A. Andriollo and M. Medina, Inorg. Chem., 25 (1986) 1106.
[20] M.A. Esteruelas, M.P. García, A.M. López, L.A. Oro, N. Ruiz, C. Schlünken, C. Valero and H. Werner, Inorg. Chem., 31 (1992) 5580.
[21] R.A. Sánchez-Delgado, W. Lee, S.R. Choi, Y. Cho and M.-J. Jun, Trans. Met. Chem., 16 (1981) 241.
[22] M.A. Esteruelas and H. Werner, J. Organomet. Chem., 303 (1986) 221.
[23] H. Werner, M.A. Esteruelas, U. Meyer and B. Wrackmeyer, Chem. Ber., 120 (1987) 11.
[24] M.A. Esteruelas, E. Sola, L.A. Oro, U. Meyer and H. Werner, Angew. Chem., Int. Ed. Engl., 27 (1988) 1563.
[25] M.A. Esteruelas, L.A. Oro and C. Valero, Organometallics, 10 (1991) 462.
[26] H. Werner, M.A. Esteruelas and H. Otto, Organometallics, 5 (1986) 2295.
[27] A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sánchez-Delgado, E. Sola, C. Valero and H. Werner, J. Am. Chem. Soc., 111 (1989) 7431.
[28] M.A. Esteruelas, C. Valero, L.A. Oro, U. Meyer and H. Werner, Inorg. Chem., 30 (1991) 1159.
[29] M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner and U. Meyer, J. Mol. Catal., 45 (1988) 1.
[30] M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner and U. Meyer, J. Mol. Catal., 53 (1989) 43.
[31] H. Werner, U. Meyer, M.A. Esteruelas, E. Sola and L.A. Oro, J. Organomet. Chem., 366 (1989) 187.
[32] M.A. Esteruelas, F.J. Lahoz, J.A. López, L.A. Oro, C.Schlünken, C. Valero and H. Werner, Organometallics, 11 (1992) 2034.
[33] J. Espuelas, M.A. Esteruelas, F.J. Lahoz, L.A. Oro and C. Valero, Organometallics, 12 (1993) 663.
[34] M.A. Esteruelas, L.A. Oro and C. Valero, Organometallics, 11 (1992) 3362.
[35] M. Aracama, M.A. Esteruelas, F.J. Lahoz, J.A. López, U. Meyer, L.A. Oro and H. Werner, Inorg. Chem., 30 (1991) 288.
[36] M.A. Esteruelas, Y. Jean, A. Lledós, L.A. Oro, N. Ruiz and F. Volatron, Inorg. Chem., 33 (1994) 3609.
[37] M.A. Esteruelas, L.A. Oro and N. Ruiz, Organometallics, 13 (1994) 1507.
[38] (a) C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini and A. Polo, Organometallics, 12 (1993) 3753; (b) P. Barbaro, C. Bianchini, M. Peruzzini, A. Polo, F. Zanobini, and P. Frediani Inorg. Chim. Acta, 220 (1994) 5.
[39] E.N. Jacobsen, I. Markó, W.S. Mungall, G. Schröder and K.B. Sharpless, J. Am. Chem. Soc., 110 (1988) 1968.
[40] J.S.M. Wai, I. Markó, J.S. Svendsen, M.G. Finn, E.N. Jacobsen and K.B. Sharpless, J. Am. Chem. Soc., 111 (1989) 1123.
[41] L. Wang and K.B. Sharpless, J. Am. Chem. Soc., 114 (1992) 7568.
[42] D. Xu, G.A. Crispino and K.B. Sharpless, J. Am. Chem. Soc., 114 (1992) 7570.
[43] R.P. Ferrari and G.A. Vaglio, Inorg. Chim. Acta, 20 (1976) 141.
[44] G.A. Vaglio, O. Gambino, R.P. Ferrari and G. Cetini, Inorg. Chim. Acta, 7 (1973) 193.
[45] Y. Shvo and R.M. Laine, J. Chem. Soc., Chem. Commun., (1980) 753.
[46] H.C. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, J. Am. Chem. Soc., 99 (1977) 8323.
[47] A.D. King, R.B. King and D.B. Yang, J. Chem. Soc., Chem. Commun., (1980) 526.
[48] M.G. Thomas, B.F. Beier and E.L. Muetterties, J. Am. Chem. Soc., 98 (1976) 1296.
[49] J.B. Keister and J.R. Shapley, J. Am. Chem. Soc., 98 (1976) 1056.
[50] (a) B. Besson, A. Choplin, L. D'Ornelas and J.-M. Basset, J. Chem. Soc., Chem. Commun., (1982) 843; (b) A. Choplin, B. Besson, L. D'Ornelas, R.A. Sánchez-Delgado and J.-M. Basset, J. Am. Chem. Soc., 110 (1988) 2783.
[51] J.L. Zuffa and W.L. Gladfelter, J. Am. Chem. Soc., 108 (1986) 4669.
[52] R.A. Sánchez-Delgado, J. Puga and M. Rosales, J. Mol. Catal., 24 (1984) 221.
[53] R.A. Sánchez-Delgado, A. Andriollo, J. Puga and G. Martin, Inorg. Chem., 26 (1987) 1867.