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Chemoselective reduction of α,β-unsaturated ketones catalyzed by transition metal complexes with polydentate ligands ☆

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Abstract

This paper reviews the catalytic activity of various Group 8 and 9 metal complexes stabilized by polydentate ligands in hydrogen-transfer reductions of α,β-unsaturated ketones. Bi- and tri-dentate ligands with mixed P,N, $-P_2N$ and P_2N_2 donor atom sets are appropriate for the synthesis of efficient iridium catalysts capable of selectively reducing α-β-unsaturated ketones to allylic alcohols. Chemoselective catalysts containing the metals of the iron triad are obtained with the tripodal tetradentate $P(CH_2CH_2PPh_2)_3$. Activity, chemoselectivity and catalysis mechanisms are compared and contrasted within the various types of complex.

Keywords: Selective reduction; Iridium; α,β-unsaturated ketones; Ruthenium; Osmium; Iron

1. Introduction

Metal-catalyzed hydrogen-transfer reductions of unsaturated organic substrates are of both considerable practical and fundamental importance. Practical motivations arise from the fact that such reactions are convenient in large-scale synthesis because there is no need to employ a high dihydrogen pressure or to use hazardous reducing agents. From the fundamental perspective, reduction reactions of unsaturated organic substrates play a key role in the understanding of homogeneous catalytic reactions, particularly of the factors that control process selectivity.

Among reducible substrates those containing both a carbonyl group and a carbon–carbon double bond, such as α,β-unsaturated ketones are very important. The ability to reduce only one group (especially the carbonyl), leaving the other unaffected, is a challenging task in organic synthesis, particularly for the preparation of pharmaceutical and agrochemical products.

The transfer hydrogenation with alcohols of α,β-unsaturated ketones is efficiently catalyzed by a restricted number of transition-metal complexes with Zr, Hf, Ru, Os, or Ir [1] which are known to bring about the chemoselective catalytic reduction of the C=O group which is less easily reduced than the double bond. Very selective catalytic reduction of α,β-unsaturated ketones is still a difficult process.

We have previously shown [1e] that in the hydrogenation of conjugated unsaturated ketones, high selectivity in unsaturated alcohols can be obtained by using iridium–phosphine complexes as catalysts. From our results, a major conclusion may be drawn: iridium–phosphine systems are flexible catalysts for the hydrogenation of this type of substrate. By employing a suitable phosphine of appropriate bulk and choosing a correct P : Ir ratio, the selectivity of the reduction can be controlled, so that either the carbon–carbon double bond or the carbonyl group can be reduced in high yield. We have also proved that $[H_5IrP_2]$ (P = monophosphine) is the active species for the reduction of the carbon–carbon double bond, while the trihydrido species $[H_3IrP_3]$ is responsible for the formation of the allylic alcohols. These results clearly showed that when using dihydrogen as reducing agent the selectivity

☆ Dedicated to Prof. Fausto Calderazzo on the occasion of his 65th birthday

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was mainly defined by the steric requirements of the coordinated phosphines. However, the same type of catalysts did not show any selectivity in the reduction of α,β-unsaturated ketones in hydrogen transfer reduction using propan-2-ol as reducing agent.

In such a system anchimeric assistance by the methoxy group of 2-anisylphosphine [$(2\text{-}MeOC_6H_4)_3P$] was found to play a key role [2] in determining the selectivity of iridium complexes in the reduction of α,β-unsaturated aldehydes to allylic alcohols. Such chemoselectivity was proposed to be related to the coordination of the methoxo group, which increases the electron density at iridium and therefore enhances the nucleophilic character of the coordinated hydride formed in the course of the reaction.

This effect was expected to be enhanced by replacing the oxygen atom with a nitrogen donor atom, as in the "hybrid" amino-phosphine (P)-NMe_2 [$(o\text{-}Me_2NC_6H_4)(C_6H_5)_2P$] [3]. Therefore we decided to develop the use of aminophosphines in iridium-assisted reduction of α,β-unsaturated ketones via hydrogen transfer. The results obtained over the last few years are summarized here.

2. Hydrogen transfer reactions using iridium catalysts stabilized by coordinated aminophosphines

Reaction of $[\{Ir(cod)(OMe)\}_2]$ (cod = cycloocta-1,5-diene) with (P)–NMe_2 (P/Ir = 2 in benzene) [(P)–NMe_2 = 1,2-$Ph_2PC_6H_4NMe_2$], gives the hydride complex [HIr(cod){(P)–NMe_2}], probably via β-hydrogen elimination from the methoxo ligand [4]. The monohydridic species [{HIr(cod)(P)-NMe_2}] reacts further with an excess of phosphine in the presence of hydrogen according to the following equations.

$$[IrH(cod)\{(P)\text{–}NMe_2\}] \xrightarrow[80°C]{H_2,\ P\text{–}NMe_2} [H_2\overline{Ir\{(P)\text{–}NCH_2Me\}}\{(P)\text{–}NMe_2\}] \quad (1)$$

$$\xrightarrow{CH_2Cl_2} [\{H\overline{IrCl(P)\text{–}NCH_2Me}\}\{(P)\text{–}NMe_2\}] \quad (2)$$

The crystal structure of compound [{$H\overline{IrCl(P)\text{–}NCH_2}$-Me}{(P)–$NMe_2$}] **2** is shown in Fig. 1. The most interesting feature of this compound is the formation of a six-membered chelate ring formed by oxidative cleavage of the *N*-Methyl C–H bond.

The (P)–NMe_2 we used creates an electron-rich metal centre, which is capable of activating a C–H bond via a three-centred transition state [5,6]. High electron density on the metal is expected, by enhancing the nucleophilic character of the coordinated hydride, to promote its selective attack on the carbon atom of the keto group of an organic substrate, even in the presence of other reducible functions. Complex **1**

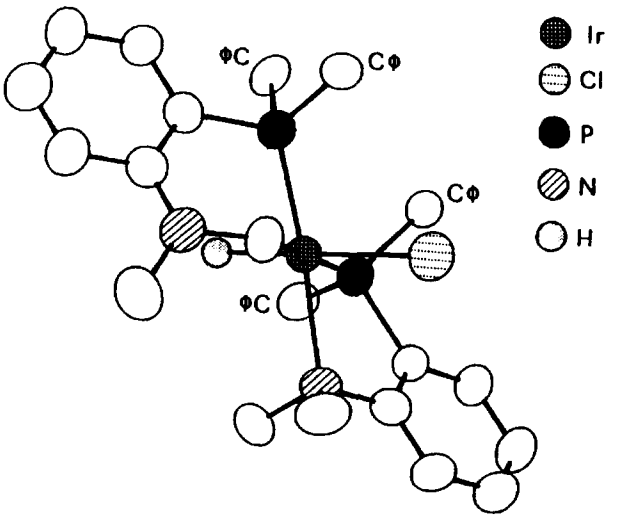
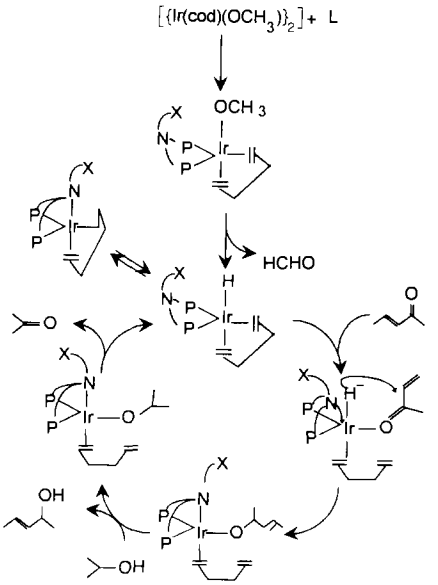


Fig. 1. Crystal structure of [{HIrCl(P)–NCH_2Me}{(P)–NMe_2}] **2**.

proved to be a highly selective catalyst for the hydrogen-transfer reduction of α,β-unsaturated ketones to allylic alcohols using propan-2-ol as hydrogen donor.

An important point of the reduction cycle catalyzed by **1** is an "arm-off" mechanism involving the amino group which appears to play a key role in determining the selectivity of the system. The reaction starts with a reductive C–H bond-coupling step promoted by interaction with the unsaturated substrate to be reduced. Later, recoordination of the nitrogen atom of the aminophosphine promotes the selective migration of the hydride to the carbonyl group (see Scheme 1 which illustrates this mechanism for a similar system). Both the activity and selectivity are remarkably high, supporting the hypothesis that one of the main factors in



Scheme 1.

determining the selectivity in such reductions is the degree of the nucleophilic character of the coordinated hydride [7]. Thus, high electron density at the metal seems to be an essential requisite for catalysts capable of selectively reducing α,β-unsaturated ketones to unsaturated alcohols via hydrogen transfer. The chemoselectivity has been related to the ability of electron-rich metal species to form M–H bonds exhibiting remarkable hydridic character [1c]. For this reason, it is not incidental that iridium and tertiary phosphines contribute the essential ingredients in several catalysis systems for such reactions [8]. However, mixed *N,P*-donors are also efficient in the chemoselective reduction of α,β-unsaturated ketones. In our opinion, the combination of soft and hard donor atoms, as occurs in aminophosphines, favours the creation of free coordination sites by the decoordination of either the phosphorus or nitrogen donor depending on the formal oxidation state of the metal during the catalysis cycle. We therefore decided to design new iridium catalysts containing polydentate ligands where the number of phosphorus donors is greater than that of nitrogen donors [9]. Such polydentate ligands, particularly those having three or more donor atoms, were also expected to offer further advantages over mono- or bi-dentate ligands [10] by providing a higher nucleophilicity of the metal and a better control of the stereochemistry and stoichiometry of the resulting complexes.

Two molecules that combine the "polydentate ligand advantages" with the presence of both phosphorus and nitrogen donors are the potentially tridentate and tetradentate ligands $^{n}Pr–N(CH_2CH_2PPh_2)_2$, *N,N*-bis[2-(diphenylphosphino)ethyl]-*n*-propylamine, PNP, and $Et_2NCH_2CH_2N(CH_2CH_2PPh_2)_2$, [*N,N*-bis(2-(diphenylphosphino)ethyl)-*N*-2-(diethylamino)ethylamine], P_2N_2.

Treatment of $[\{Ir(cod)(OMe)\}_2]$ with PNP or P_2N_2 gives a pale yellow solution from which crystals of $[(PNP)Ir(\sigma,\eta^2\text{-}C_8H_{13})]$ or of the analogous P_2N_2 compound are obtained (Scheme 1).

Formaldehyde is formed in the course of the reaction, indicating that a β-H elimination reaction from the coordinated methoxo group has occurred. The molecular structure of the PNP derivative is shown in Fig. 2.

In keeping with the crystal structure, the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 at 198 K exhibits an AB spin system with δP_A 13.30, δP_B 10.90 ppm and $J(P_AP_B) = 85.5$ Hz. Such a pattern is consistent with the inequivalence of the phosphorus of PNP (Fig. 3).

The $^{31}P\{^1H\}$ NMR spectra in Fig. 3 show that the temperature not only affects the NMR parameters but also promotes a thermal, reversible transformation of $[(PNP)Ir(\sigma,\eta^2\text{-}C_8H_{13})]$ into a novel species. An appreciable amount of such species begins to form at 248 K, as shown by the singlet at 0.94 ppm. The A_2 pattern is

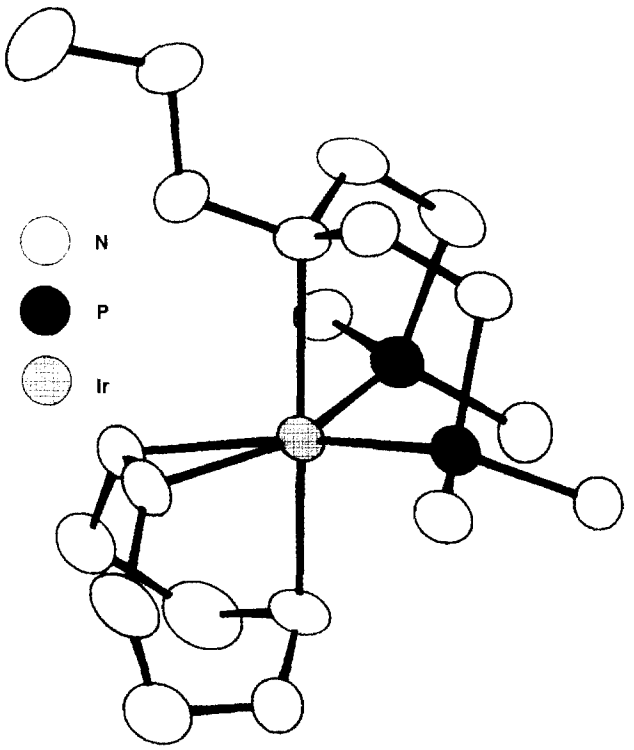


Fig. 2. Crystal structure of $[(PNP)Ir(\sigma,\eta^2\text{-}C_8H_{13})]$.

consistent with the magnetic equivalence of the two phosphorus nuclei of PNP. Information on the new species is provided by variable-temperature ^1H NMR spectroscopy. At 248 K, the formation of the new species is accompanied by the appearance of a triplet at −13.51 ppm [$J(HP) = 21.3$ Hz]. The position, the multiplicity, and the $J(HP)$ values of this resonance are diagnostic of a terminal hydride *cis* to two equivalent phosphorus nuclei [11].

In view of an X-ray analysis on the $\sigma,\eta^2\text{-}C_8H_{13}$ precursor as well as the variable-temperature NMR studies, it is concluded that above 248 K $[(PNP)Ir(\sigma,\eta^2\text{-}C_8H_{13})]$ is in equilibrium with the isomer $[(PNP)IrH(\eta^4\text{-cod})]$ via a β-H elimination/hydride migration process as shown in the lower part of Scheme 2.

The reaction of isolated $[(PNP)Ir(C_8H_{12})]^+$ (or of $[(P_2N_2)Ir(C_8H_{12})]^+$) with an equimolecular amount of $Li[HBEt_3]$ yields the σ-cyclooctenyl compounds quantitatively, demonstrating indirectly that the proposed mechanism leading to formation of $[(PNP)Ir(\sigma,\eta^2\text{-}C_8H_{13})]$ from $[\{Ir(cod)(OMe)\}_2]$ and PNP (or P_2N_2) is correct (Scheme 2). Such a mechanism must therefore involve the cleavage of the dimeric structure of $[\{Ir(cod)(OMe)\}_2]$ by PNP or P_2N_2 to give mononuclear species containing a terminal methoxo ligand. The latter readily β-eliminates formaldehyde and thus generates a terminal hydride.

According to the mechanism in Scheme 2, the bridging nitrogen atom in both PNP and P_2N_2 plays a

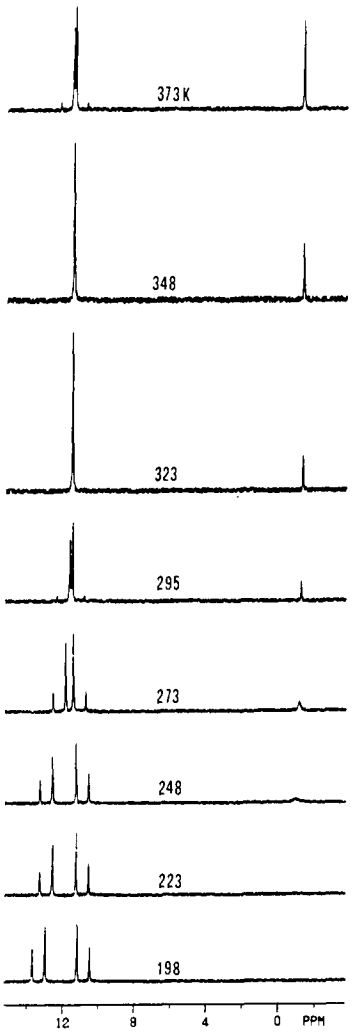
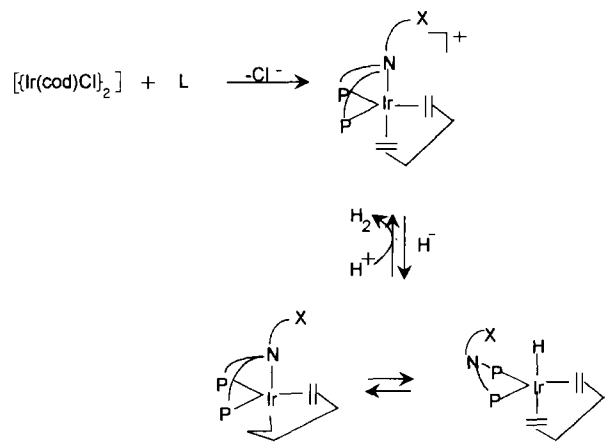


Fig. 3. Variable temperature $^{31}P\{^1H\}$ NMR spectra of 1:1 mixture of $[Ir(cod)(OMe)]_2$ and P_2N_2 in toluene-d_8 (85% H_3PO_4 ref.).

determining role in the interconversion of σ-cyclooctenyl and (hydride)(η^4-cod) structures. In particular, the β-H elimination reaction involving the Ir-



Scheme 2.

σ-cyclooctenyl moiety would be made possible just by the facile cleavage of the N–Ir bond. In order to verify the role played by the hard N donor, we have replaced PNP and P_2N_2 by the tripodal $MeC(CH_2PPh_2)_3$, (triphos), and we have been able to synthesize the complex [(triphos)Ir(σ,η^2-C_8H_{13})]. This complex is quite stable even in refluxing THF or toluene solutions, providing indirect evidence that the β-H elimination/hydride migration mechanism undergone by PNP and P_2N_2 complexes is determined by the presence of a nitrogen donor in the polydentate ligand.

The reduction of benzylideneacetone was carried out using propan-2-ol or cyclopentanol as hydrogen donors. Two different catalyst systems were investigated: isolated [(PNP)Ir(σ,η^2-C_8H_{13})] (or the P_2N_2 homologue) and a 1:1 mixture of $[\{Ir(cod)(OMe)\}_2]$ and PNP (or P_2N_2) in the appropriate alcohol prepared in situ.

The results obtained show that, regardless of the catalytic system, the P_2N_2 catalysts are invariably more active than those with PNP. An induction period in the conversion is observed when the reaction is carried out at 83°C in propan-2-ol, which disappears at 140°C using cyclopentanol as the donor.

These results are consistent with the solution chemistry of these compounds as well as the reaction path reported in Scheme 1. This involves reaction of $[\{Ir(cod)(OMe)\}_2]$ with PNP or P_2N_2 to give five-coordinate intermediate species through the cleavage of the methoxo bridge [12]. At this stage, we suggest that the unsaturated ketone approaches the complex, displacing one olefin bond. This is followed by selective transfer of hydride to the carbonyl group of coordinated ketone promoted by recoordination of the nitrogen donor, and is the likely key step of the reaction. The intermediate reacts with propan-2-ol and as a result, the Ir–O bond is cleaved and free unsaturated alcohol is formed together with an *O*-isopropoxo complex. The final step restores the parent hydride via β-H elimination, thereby closing the catalysis cycle.

3. Hydrogen transfer reactions using catalysts stabilized by tripodal tetraphosphines

We have reported above that selective reduction of the carbonyl group in α,β-unsaturated ketones catalyzed by iridium complexed by PNP or PN is brought about by the presence of a donor atom capable of undergoing an "arm-off" mechanism. In contrast, no catalytic activity is observed using a polyphosphine. In order to obtain more information [13] on the effect of ligands having only phosphorus atoms for the formation of selective catalysts, we have compared the behaviour of isostructural iron(II), ruthenium(II), and osmium(II) complexes of the formula $[(PP_3)M(H)(H_2)]$

BPh_4, [M = Fe, Ru, or Os; $PP_3 = P(CH_2CH_2PPh_2)_3$]. The compounds are non-classical trihydrides, displaying identical structures where the metal is octahedrally coordinated by the four phosphorus atoms of the tripodal ligand, by a terminal hydride ligand, and by a side-on-bonded dihydrogen molecule *trans* to the bridgehead phosphorus atom. X-ray structure analyses have been carried out on all the compounds [14]. These compounds have previously been found to catalyze efficiently the selective hydrogenation of 1-alkynes to alkenes [Fe [15] and Ru [16]] and the stereoselective dimerization of 1-alkynes to (Z)-1,4-disubstituted butenynes (Ru and Os) [17].

Both the steric crowding at the metal, which increases in the order Fe > Ru > Os, and/or the nature of the metal seem to be of crucial importance in determining selective pathways. Both these factors are also determining in driving the selectivity of the hydrogen-transfer reactions, and we have shown that the iron and osmium complexes exhibit opposite chemoselectivity.

4. Hydrogen-transfer reductions assisted by Iron(II), Ruthenium(II) and Osmium(II) complexes stabilized by $P(CH_2CH_2PPh_2)_3$

4.1. Iron(II) system: $[(PP_3)Fe(H)(H_2)]BPh_4$

The hydrogen-transfer reduction of benzylideneacetone (PhCH=CHCOMe) is catalyzed by the iron system with good catalytic activity and excellent chemoselectivity, the only product being the corresponding unsaturated alcohol. Reactions are performed using either propan-2-ol or cyclopentanol as hydrogen donors and THF or 1,4-dioxan as solvents. The catalytic reactions are performed under argon. When dinitrogen is employed, a marked loss in the catalytic activity takes place. An even more dramatic effect is observed when the reactions are performed in the presence of H_2, as the catalytic activity is almost completely suppressed. Similar behaviour is shown also by the Ru and Os systems. Surprisingly, the reduction of other acyclic unsaturated ketones to give the saturated ketone proceeds at the C=C bond which is not subsequently reduced. The most impressive observation is the change in selectivity a substituting a methyl by a phenyl group (benzylideneacetone, which gives only unsaturated alcohol compared to chalcone, which gives only saturated ketone). Both steric and electronic factors (i.e. the larger size of the phenyl substituent and the lower polarization of the keto group in chalcone) may be responsible for such a change in selectivity.

Aldehydes are not reduced by this system, but this is not surprising as they undergo fast disproportionation reactions with irreversible formation of stable iron(II) η^2-*O*,*O*-carboxylato complexes of the formula $[PP_3Fe(O_2CR)]^+$ [18].

4.2. Ruthenium(II) system: $[(PP_3)Ru(H)(H_2)]BPh_4$

The hydrogen-transfer reduction of benzylidenacetone is catalyzed by this system with high catalytic activity and good chemoselectivity, the predominant product being the corresponding unsaturated alcohol. Other products are the saturated ketone and the saturated alcohol. The highest chemoselectivity (up to 90%) is obtained at 30–40°C. At higher temperatures, the reactions are very fast, and the unsaturated alcohol formed is rapidly reduced to a saturated alcohol. Aldehydes, such as benzaldehyde and cinnamaldehyde, are not reduced, and they appear to react irreversibly with the ruthenium catalyst, as inferred from competition studies.

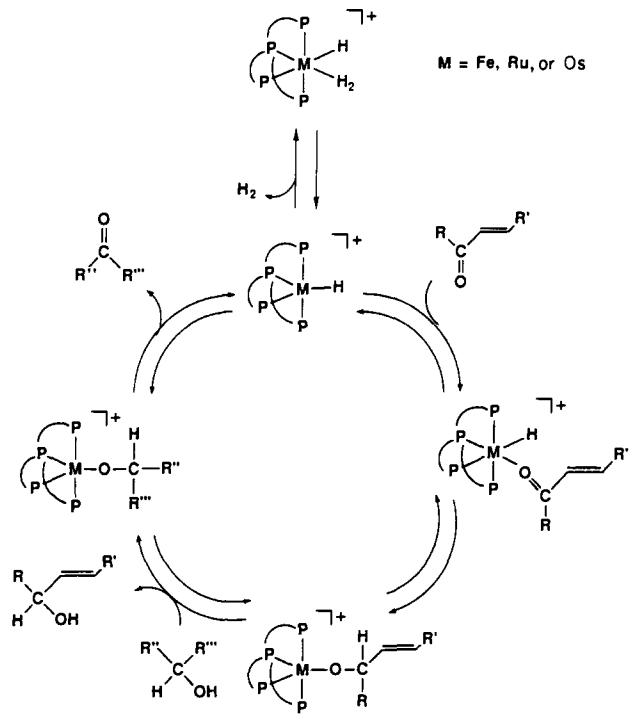
Propan-2-ol is dehydrogenated in the course of the reaction to give acetone which, like acyclic ketones, has been found to react with our ruthenium catalyst in a disproportionation reaction, resulting in slow, irreversible deactivation of the system because of formation of ruthenium carboxylates of the formula $[(PP_3)Ru(\eta^2\text{-}O,O\text{-}O_2CR)]^+$ [18].

Such a deactivation is a minor disadvantage when the substrate reduction is fast, whereas in some cases deactivation of the catalyst can be competitive with substrate reduction and, therefore, complete conversion is not obtained. The ruthenium catalyst system is very robust. A number of consecutive reactions can be performed using the same catalyst with no appreciable decay of activity. This does not occur with the iron catalyst precursor, which undergoes considerable deactivation during each run.

4.3. Osmium(II) system: $[(PP_3)Os(H)(H_2)]BPh_4$

Hydrogen-transfer reactions catalyzed by the Os II system must be performed in pure donor because the presence of a cyclic ether (THF, 1,4-dioxan) inhibits the catalytic activity. Both propan-2-ol and cyclopentanol are suitable hydrogen donors, the reactions being generally slightly faster in the case of propan-2-ol, probably because of the lower inhibiting effect of acetone, as compared to cyclopentanone. Acetone can readily be evaporated off under the reaction conditions (80°C). Like ruthenium, the osmium catalyst is very stable and several catalytic cycles can be accomplished providing the system is recharged with the substrate and the hydrogen donor. The activity is generally lower than with ruthenium, as would be expected for a 5d metal.

α,β-Unsaturated ketones are generally reduced with this system to the corresponding saturated ketones, which are subsequently reduced to saturated alcohols.



Scheme 3.

A number of experiments were performed using substituted allyl alcohols as substrates in order to ascertain whether an isomerization process was operative. The unsaturated alcohol PhCH=CHCH(OH)Me (reduction product of benzylideneacetone) is slowly isomerized to the saturated ketone by the Os II system.

5. Mechanism of reduction

Reactivity studies have clearly shown that the solution chemistry of these non-classical trihydrides is dominated by the different metal–dihydrogen bond strengths, which increase in the order Ru ≪ Fe < Os [19]. Displacement of the dihydrogen molecule by neutral L such as N_2, CH_3CN, PR_3, or CO to give $[(PP_3)M(H)(L)]^+$ is a feasible reaction for all compounds. However, more drastic conditions are generally required for Fe and Os than for Ru.

In light of the NMR evidence, there is little doubt that these compounds are catalyst precursors for the hydrogen-transfer reduction of benzylideneacetone, the real catalytic species being the monohydrides $[(PP_3)MH]^+$. These are coordinatively and electronically unsaturated species and, therefore, susceptible to attack by ketones.

Although we have provided evidence for η^1-*O*-coordination of benzylideneacetone only for osmium [13], it is reasonable that iron and ruthenium also initially coordinate the unsaturated ketone via the oxygen atom *cis* position to the terminal hydride. Provided this initial step occurs for all metals, a common catalytic cycle can be proposed (Scheme 3). This involves migration of hydride from metal to coordinated ketone to give an alkoxo complex. Reaction of the last species with the hydrogen donor (e.g. propan-2-ol) cleaves the M–O bond with consequent formation of free allyl alcohol and an isopropox complex. Finally, the unsaturated hydride is regenerated via a β-H elimination reaction, thereby closing the catalysis cycle.

6. Conclusions

The mechanism of the selective reduction of α,β-unsaturated ketones in hydrogen transfer appears to be dependent on the basicity of the ligands as they produce an electron-rich metal which promotes selective transfer of the hydride onto the carbonyl group. This effect can be produced either by using a mixed *N*, *P*-donor or by using strong σ-donor polydentate phosphines the main difference between the two systems being the mechanism of formation of a coordination vacancy at the metal. In mixed *N*, *P*-donors, a free coordination site is generated via an "arm-off" mechanism. In polyphosphine metal complexes, the presence of the strong phosphorus donors connected by alkyl chains (chelate effect) inhibits "arm-off mechanisms". In this case, a coordination vacancy can easily be generated by loss of a weakly bound ligand (i.e. H_2) from the metal precursor.

Acknowledgments

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References

[1] (a) Y. Sasson and J. Blum, *Tetrahedron Lett.*, (1971) 2167; (b) Y. Sasson and J. Blum, *J. Org. Chem.*, *40*, (1976) 1887; (c) T. Nakano, S. Umano, Y. Kino, Y. Ishii and M. Ogano, *J. Org. Chem.*, *53* (1988) 3752; (d) R.A. Sanchez-Delgado, A. Andriollo, E. Gonzales, N. Valencia, V. Leon and J. Espidel, *J. Chem. Soc., Dalton Trans.*, (1986) 1859; (e) E. Farnetti, J. Kaspar, R. Spogliarich and M. Graziani, *J. Chem. Soc., Dalton Trans.*, (1988), 947; (f) M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner and U. Moyer, *J. Mol. Catal.*, *45* (1988) 1; (g) E. Farnetti, N.V. Gulati and M. Graziani, *Gazz. Chim. Ital.*, *123*, (1993) 165.

[2] M. Visintin, R. Spogliarich, J. Kaspar and M. Graziani, *J. Mol. Catal.*, *32* (1985) 349.

[3] H.P. Fritz, I.R. Gordon, K.E. Schwarzhans and L.M. Venanzi, *J. Chem. Soc.*, (1965) 5210.

[4] M.J. Fernandez, M.A. Esteruelas, M. Covarrubias, and L.A. Oro, *J. Organomet. Chem.*, *316* (1986) 343.
[5] J.M. Buchanan, J.M. Stryker, and R.G. Bergman, *J. Am. Chem. Soc.*, *108* (1986) 1537.
[6] E. Farnetti, J. Kaspar and M. Graziani, *J. Mol. Catal.*, *63* (1990) 5.
[7] E. Farnetti, G. Nardin and M. Graziani, *J. Chem. Soc., Chem. Commun.*, (1989) 1264.
[8] T.B. Rauchfuss and D.M. Roundhill, *J. Am. Chem. Soc.*, *96* (1974) 3098.
[9] C. Bianchini, E. Farnetti, M. Graziani, G. Nardin, A. Vacca and F. Zanobini, *J. Am. Chem. Soc.*, *112* (1990) 9190.
[10] E.C. Ayela and D.W. Meek (eds.), *Catalytic Aspects of Metal Phosphine Complexes, Advances in Chemical Series*, American Chemical Society, 1982, 196.
[11] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, P. Frediani and J.A. Ramirez, *Organometallics*, *7* (1988) 1704.
[12] M.J. Fernandez, M.A. Esteruelas, M. Covarrubias, and L.A. Oro, *J. Organomet. Chem.*, *316* (1986) 343.
[13] C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini, and A. Polo, *Organometallics*, *12* (1993) 3753.
[14] C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca, and F. Zanobini, *Inorg. Chem.*, *32* (1993) 2366.
[15] C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M.A. Esteruelas, and L.A. Oro, *Organometallics 11* (1992) 138.
[16] C. Bianchini, C. Bohanna, M.A. Esteruelas, P. Frediani, A. Meli, L.A. Oro, and M. Peruzzini, *Organometallics 11* (1992) 3838.
[17] C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani, and A. Albinati, *J. Am. Chem. Soc.*, *113* (1991) 6463; P. Barbaro, C. Bianchini, M. Peruzzini, A. Polo and F. Zanobini, *Inorg. Chim. Acta 220* (1994) 5.
[18] C. Bianchini, E. Farnetti, P. Frediani, M. Graziani, M. Peruzzini and A.J. Polo, *J. Chem. Soc., Chem. Commun.*, (1991) 1336.
[19] J. Eckert, A. Albinati, R.P. White, C. Bianchini, and M. Peruzzini, *Inorg. Chem. 31* (1992) 4241.