Chemoselective Hydrogen-Transfer Reduction of α,β-Unsaturated Ketones Catalyzed by Isostructural Iron(II), Ruthenium(II), and Osmium(II) *cis* Hydride η^2-Dihydrogen Complexes

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The nonclassical trihydrides $[(PP_3)M(H)(\eta^2\text{-}H_2)]BPh_4$ (M = Fe, Ru, Os) are efficient catalyst precursors for the reduction of α,β-unsaturated ketones *via* hydrogen-transfer from secondary alcohols [$PP_3 = P(CH_2CH_2PPh_2)_3$]. α,β-Unsaturated ketones bearing bulky substituents at the double bond (*i.e.* benzylideneacetone) are chemoselectively reduced to allylic alcohols by using either the iron or the ruthenium catalyst. In contrast, the osmium system catalyzes the reduction of α,β-unsaturated ketones to saturated ketones *via* isomerization of the initially produced allylic alcohols. A number of reducible substrates including various unsaturated and saturated ketones, aldehydes, alkenes, and alkynes have been studied in order to get information on the steric and electronic factors which may affect the interaction of the substrate with the metal center and, thus, control the selectivity of the hydrogen-transfer reductions. Evidence is provided for the formation of an η^1-*O*-benzylideneacetone complex of the formula $[(PP_3)Os(H)\{\eta^1\text{-}OCMe(CH{=}CHPh)\}]BPh_4$ which has been characterized by multinuclear NMR spectroscopy. The latter compound and the related complex $[(PP_3)Os(H)(\eta^1\text{-}OCMe_2)]BPh_4$ have been used in a number of reactions. As a result, valuable information has been obtained which allows one to propose catalytic cycles for the hydrogen-transfer reduction of α,β-unsaturated ketones to unsaturated alcohols assisted by the Fe and Ru complexes, and for the isomerization of allylic alcohols to saturated ketones catalyzed by the Os complex.

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 since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents. From the fundamental perspectives, reduction reactions of unsaturated organic substrates play a key role in the understanding of homogeneous catalytic reactions, particularly of the factors that control the selectivity of a process.

Among the various reducible substrates of great relevance are those containing both a carbonyl group and a C=C bond such as α,β-unsaturated ketones. Indeed, the capability of reducing only one group (especially the former), leaving the other one 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, and Ir.[1] An even lower number of metal complexes containing Zr, Hf, or Ir, are known to bring about the chemoselective catalytic reduction of the C=O group which is less easily reducible than the double bond.[1d,f,h,m] Highly selective catalytic reduction of α,β-unsaturated ketones is therefore an open question.

In this paper, we compare and contrast the behavior of isostructural iron(II), ruthenium(II), and osmium(II) complexes of the formula $[(PP_3)M(H)(H_2)]BPh_4$ as homogeneous catalysts in the reduction of α,β-unsaturated ketones *via* hydrogen-transfer from either propan-2-ol or cyclopentanol and with no need of a basic cocatalyst [M = Fe, **1**; Ru, **2**; Os, **3**; $PP_3 = P(CH_2CH_2PPh_2)_3$]. A detailed study has been carried out on the model substrate benzylideneacetone (PhCH=CHCOMe), but useful comparisons have been made with other unsaturated ketones.

Compounds **1–3** are nonclassical trihydrides displaying an identical structure where the metal center 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 bridge-

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(1) (a) Sasson, Y.; Blum, J. *Tetrahedron Lett.* **1971**, 2167. (b) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887. (c) Sanchez-Delgado, R. A.; Andriollo, A.; Gonzales, E.; Valencia, N.; Leon, V.; Espidel, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1859. (d) Farnetti, E.; Kaspar, J.; Spogliarich, R.; Graziani, M. *J. Chem. Soc., Dalton Trans.* **1988**, 947. (e) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (f) Nakano, T.; Umano, S.; Kino, Y.; Ishii, Y.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3752. (g) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43. (h) Bianchini, C.; Farnetti, E.; Graziani, M.; Nardin, G.; Vacca, A.; Zanobini, F. *J. Am. Chem. Soc.* **1990**, *112*, 9190. (i) Chowdhuri, R. L.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063. (j) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (k) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362. (l) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1992**, *11*, 702. (m) Farnetti, E.; Gulati, N. V.; Graziani, M. *Gazz. Chim. Ital.* **1993**, *123*, 165.

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head phosphorus atom.[2-4] X-ray structure analyses have been carried out for all compounds.[4,5]

The use of 1–3 in homogeneous catalysis is in an early stage of development, and a few results have already appeared. In particular, the compounds have been found to efficiently catalyze the selective hydrogenation of 1-alkynes to alkenes (Fe,[6]Ru[7]) and the stereoselective dimerization of 1-alkynes to *Z*-1,4-disubstituted butenynes (Ru,[8]Os[9]). Of crucial importance in determining selective pathways seems to be either the steric crowding at the metal center, which increases in the order Fe > Ru > Os, or the nature of the metal center. Both these factors are determinant also in driving the selectivity of the hydrogen-transfer reactions described in this paper, as we will show that the iron and osmium complexes exhibit opposite chemoselectivity. Also, unlike the Fe and Ru complexes, we will show that the Os congener is also capable of catalyzing another important reaction, namely the isomerization of allylic alcohols to saturated ketones.

Experimental Section

General Procedure. All reactions and manipulations were routinely performed under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. Tetrahydrofuran (THF) and *p*-dioxane were distilled from sodium: CH_2Cl_2 and 1,2-dichloroethane, from P_2O_5 prior to use. All other chemicals were commercial products and were used as received without further purifications. All the substrates were recrystallized or distilled over an inert atmosphere prior to use. Literature methods were used for the preparation of $[(PP_3)Fe(H)(H_2)]BPh_4$ (**1**),[2] $[(PP_3)Ru(H)(H_2)]BPh_4$ (**2**),[3] $[(PP_3)Os(H)(H_2)]BPh_4$ (**3**),[4] $[(PP_3)Os(H)(N_2)]BPh_4$ (**4**),[4] $[(PP_3)Os(H)(\eta^1\text{-}OCMe_2)]BPh_4$ (**6**),[4] and crotonophenone.[10] Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H NMR spectra were recorded on a Bruker ACP 200 (200.13-MHz) spectrometer. ^1H NMR shifts were measured relative to residual ^1H resonances in the deuterated solvent (CD_2Cl_2, δ 5.32 or THF-d_8, δ 1.87). $^{31}P\{^1H\}$ NMR spectra were recorded on either Varian VXR 300 or Bruker ACP 200 instruments operating at 121.42 or 81.01 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Broad band and selective $^1H\{^{31}P\}$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and BFX-5 amplifier device. The catalytic reactions were monitored by GLC on a Perkin-Elmer Sigma 3B gas chromatograph using either a Supelcowax 10 wide-bore capillary column (30 m × 0.75 mm i.d.) or a CP-Sil-5 CB wide-bore capillary column (25 m × 0.53 mm i.d.). Alternatively, the reaction products were identified by GC–MS using a Hewlett-Packard 5971 A mass detector coupled with a 5890II gas chromatograph on an SP255 capillary column (25 m × 3 μm).

Catalytic Experiments. Iron System. A three-necked thermostated glass reactor equipped with a condenser, an argon inlet, a rubber septum, and a magnetic bar was charged under argon with 48.5 mL of *p*-dioxane and 1.50 mL of propan-2-ol (or 48.2 mL of *p*-dioxane and 1.80 mL of cyclopentanol). Addition of **1** (10.49 mg, 0.01 mmol) gave a yellow solution, which was heated to 80 °C and treated with 1.0 mmol of the substrate.

Ruthenium System. The thermostated reactor described above was charged under argon with 40.5 mL of THF or *p*-dioxane and 9.50 mL of propan-2-ol (or, alternatively, with 38.5 mL of THF or *p*-dioxane and 11.30 mL of cyclopentanol). Addition of **2** (10.94 mg, 0.01 mmol) gave a pale yellow solution, which was heated to 60 °C and treated with 2.5 mmol of the substrate.

Osmium System. The thermostated reactor described above was charged with 50.0 mL of propan-2-ol (or, alternatively, with cyclopentanol). Addition of **3** (11.83 mg, 0.01 mmol) gave a pale yellow solution, which was heated to 80 °C and treated with 2.5 mmol of the substrate.

NMR Studies. Iron System. A 20-mL flask equipped with a reflux condenser, a side arm with a rubber septum, and a magnetic bar was charged under argon with a solution of **1** (50 mg, 0.048 mmol) in 3 mL of dioxane/cyclopentanol (10:3, v:v). The resulting yellow solution was heated at 80 °C for 10 min. After this time, a preheated solution of benzylideneacetone (200 mg, 1.37 mmol) (substrate to catalyst ratio = 28.7) in the same solvent mixture (3 mL) was added *via* cannula, and the reaction mixture was stirred at 80 °C. After 3 h, the reaction was quenched by both cooling down at 0 °C and bubbling N_2. An identical procedure was done for a second reaction, the only difference being the substitution of CO for N_2. A portion (0.6 mL) of each quenched mixture was sampled and transferred *via* syringe into an NMR tube containing C_6D_6 (0.5 mL) previously degassed with either N_2 or CO. $^{31}P\{^1H\}$ NMR spectra showed the formation of the monohydrido complexes $[(PP_3)Fe(H)(N_2)]BPh_4$[2] and $[(PP_3)Fe(H)(CO)]BPh_4$,[2] respectively, in *ca.* 40% yield (based on NMR integration), together with the starting complex **1** (*ca.* 30%) and several unidentified PP_3 compounds.

Ruthenium System. A reactor assembled as described above was charged with 52 mg of **2** (0.048 mmol) and benzylideneacetone (200 mg, 1.37 mmol). After workup identical with that used for the iron derivative, $^{31}P\{^1H\}$ NMR spectra showed quantitative conversion of **2** to either $[(PP_3)Ru(H)(N_2)]BPh_4$[3] or $[(PP_3)Ru(H)(CO)]BPh_4$.[3]

Osmium System. A. Reaction of $[(PP_3)Os(H)(N_2)]BPh_4$ with Benzylideneacetone. A stoichiometric amount of benzylideneacetone (6.1 mg, 0.042 mmol) was added to a CD_2Cl_2 (1 mL) solution of $[(PP_3)Os(H)(N_2)]BPh_4$ (**4**) (50 mg, 0.042 mmol) degassed with argon. The resulting pale yellow solution was transferred into a 5-mm NMR tube, and $^{31}P\{^1H\}$ and ^1H NMR spectra were immediately recorded. Quantitative conversion of **4** to the novel complex $[(PP_3)Os(H)\{\eta^1\text{-}OCMe(CH{=}CHPh)\}]BPh_4$ (**5**) was observed. $^{31}P\{^1H\}$ NMR: AMQ_2 spin system, δP_A 105.39, δP_M 24.10, δP_Q 30.36, $J(P_AP_M)$ = 12.3, $J(P_AP_Q)$ = 4.9, $J(P_QP_M)$ = 6.0 Hz. ^1H NMR: δ(Os–H) −7.22, dtd, $J(HP_M)$ = 72.6, $J(HP_Q)$ = 26.0, $J(HP_A)$ = 11.8 Hz, assigned by $^1H\{^{31}P\}$ NMR spectroscopy; $\delta(CH_3CO)$ 2.37, s; $\delta(CH{=}CH)$ 7.40, 6.74, d, J(HH) = 16.3 Hz.

B. Reaction with Benzylideneacetone in THF-d_8. On substituting THF-d_8 for CD_2Cl_2 in the above procedure did not provide NMR evidence of appreciable formation of **5**, but showed conversion of **4** to the THF adduct $[(PP_3)Os(H)(THF)]^+$.[4]

C. Reduction of Coordinated Benzylideneacetone in 5 with Propan-2-ol. A double proportion of propan-2-ol was syringed into a 5-mm NMR tube containing a solution of **5** prepared as described in procedure A. $^{31}P\{^1H\}$ NMR analysis of the resulting mixture showed disappearance of **5** and formation of the known η^1-*O*-acetone adduct $[(PP_3)Os(H)(OCMe_2)]BPh_4$ (**6**) and free $PhCH_2CH_2COMe$ (determined by either ^1H NMR spectroscopy or GC analysis by comparison with an authentic specimen).

D. Reaction of 6 with Benzylideneacetone. The η^1-acetone adduct **6** (50 mg, 0.040 mmol) was dissolved under an argon

(2) Bianchini, C.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Gazz. Chim. Ital.* **1991**, *121*, 543.
(3) Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.
(4) Bianchini, C.; Linn, K.; Masi, D.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Inorg. Chem.* **1993**, *32*, 2366.
(5) X-ray structure analyses have been carried out also for **1** and **2**. The compounds are isostructural with **3** whose molecular structure is described in ref 4.
(6) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, *11*, 138.
(7) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3838.
(8) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453.
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atmosphere into a Schlenk tube containing a CH_2Cl_2 (10-mL) solution of benzylideneacetone (60 mg, 0.41 mmol). Addition of propan-2-ol (39 μL, 0.83 mmol) resulted in formation of the saturated ketone (40% based on the amount of benzylideneacetone).

E. Isomerization of PhCH=CHCH(OH)Me to $PhCH_2CH_2COMe$ Catalyzed by 6. A 10-fold excess of the allylic alcohol (60 mg, 0.41 mmol) was dissolved in a CD_2Cl_2 solution of **6** (50 mg, 0.040 mmol) under argon. The resulting solution was transferred into a 5-mm NMR tube, which was inserted into the spectrometer preheated at 30 °C. Complete isomerization of the allylic alcohol to the corresponding ketone occurred within 3 h (^1H NMR, GC). After the reaction was quenched with carbon monoxide, $[(PP_3)Os(H)(CO)]BPh_4$[4] was recognized as the only osmium-containing species.

F. Isomerization of PhCH=CHCH(OH)Me to $PhCH_2CH_2COMe$ Catalyzed by 4. Benzylideneacetone (50 mg, 0.34 mmol), 1,2-dichloroethane (15 mL), and a stirring bar were placed in a reaction vessel fitted with a reflux condenser and a side arm with a rubber septum under argon. The vessel was immersed in a constant-temperature oil bath (80 °C). The catalyst (4.1 mg, 0.0034 mmol) was added. The reaction mixture was sampled after 1 h. GC analysis showed 90% conversion of the allylic alcohol to the saturated ketone.

G. Isomerization of *cis*-Stilbene to *trans*-Stilbene Catalyzed by 4. A stirred mixture of **4** (60 mg, 0.05 mmol) and *cis*-stilbene (90 mg, 0.50 mmol) in dichloroethane was stirred under argon at 80 °C for 1 h. GC analysis showed formation of *trans*-stilbene in an amount close to the *cis-trans* equilibrium (98 *vs* 99.4% for the *trans* isomer).

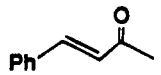
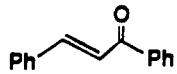
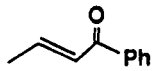
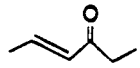
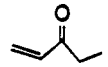
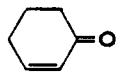
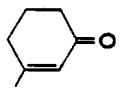
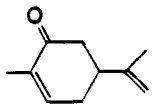
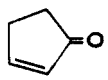
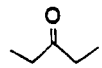
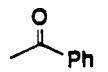
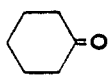
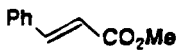
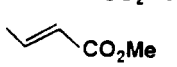
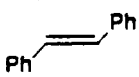
Results and Discussion

Hydrogen-Transfer Reductions Assisted by the Iron(II) Complex 1. The hydrogen-transfer reduction of benzylideneacetone (PhCH=CHCOMe) is catalyzed by **1** with good catalytic activity and excellent chemoselectivity, the only product being the corresponding unsaturated alcohol (Table I). Reactions are performed using either propan-2-ol or cyclopentanol as hydrogen donors and THF or *p*-dioxane as solvents. It is essential to use a solvent since the catalytic activity is almost completely depressed when using pure propan-2-ol or cyclopentanol. *p*-Dioxane is generally preferred over THF, as it allows one to operate at higher temperature (80 °C). Neither THF nor *p*-dioxane behave as hydrogen donors under the experimental conditions. The catalytic reactions are performed under argon atmosphere; when nitrogen is employed as the inert gas, 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 of **1** is almost completely depressed. Monitoring the reactions by GC unambiguously shows the absence of any induction period. Unless otherwise stated, these experimental observables are valid also for the reactions catalyzed by the Ru and Os congeners **2** and **3**.

Surpisingly, the reduction of other acyclic unsaturated ketones proceeds at the C=C bond, to give the saturated ketone, which is not subsequently reduced. Most impressive is the change in selectivity by substituting a methyl with a phenyl group (benzylideneacetone, entry 1, *vs* chalcone, entry 2). Both steric and electronic factors (*i.e.* the larger size of the phenyl substituent and the lower polarization of the keto group in chalcone) are probably responsible for such a selectivity change, which is observed also for Ru.[1m]

Cyclohexenone (entry 6) is reduced at both unsaturated groups with formation of the saturated ketone, which is in turn reduced to the alcohol, and the unsaturated alcohol which does not undergo further reduction. Upon an increase in the degree of substitution at the C=C bond, as in 3-methyl-2-cyclohexen-1-one (entry 7), the selectivity in unsaturated alcohol increases at the expense of the catalytic activity. In the case of carvone (entry 8), however, no reduction product is observed, most likely because of the presence of a methyl substituent in the α-position with respect to the carbonyl group. Notably, cyclopentenone (entry 9) is reduced (using propan-2-ol as the hydrogen donor) to the saturated ketone, which is then slowly reduced to cyclopentanol.

Table I. Hydrogen-Transfer Reduction Catalyzed by $[(PP_3)FeH(H_2)]BPh_4$ (1)[a]

entry		% conv (time, h)	% sat. ketone	% sat. alcohol	% unsat alcohol
1		95 (7)	0	0	95
2		30 (7)	30	0	0
3		7 (5)	7	0	0
4		19 (5)	19	0	0
5		100 (1)	100	0	0
6		72 (5)	0	44	28
7		31 (7)	0	0	31
8		0 (7)	0	0	0
9[b]		100 (3)	84	16	0
10		0 (5)		0	
11		2 (5)		2	
12		55 (5)		55	
13		0 (7)			
14		25 (7)[c]			
15		0 (7)			
16		0 (7)			

[a] Reactions conditions: [1] = 2 × 10^{-4} M; [substrate]/[1] = 100; hydrogen-donor = cyclopentanol; [hydrogen-donor]/[substrate] = 20; solvent = dioxane; T = 80 °C. [b] Hydrogen-donor = propan-2-ol. [c] Reaction product $CH_3(CH_2)_2CO_2Me$.

Complex 1 is not an efficient catalyst for the reduction of saturated ketones such as 3-pentanone and acetophenone (entries 10 and 11); a surprising exception is represented by cyclohexanone which is reduced to the corresponding alcohol (entry 12).

Interestingly, when mixtures of unsaturated and saturated ketones (typically benzylideneacetone and acetophenone) are employed, catalyst 1 selectively promotes the reduction of the enone to the corresponding unsaturated alcohol (only traces of 1-phenylethanol are detected in the reaction mixture). To the best of our knowledge, this is the first catalyst which exhibits such a substrate selectivity. In fact, the carbonyl group reduction of an unsaturated ketone is generally much more difficult to perform than the reduction of a simple ketone.[11] On the other hand, we wish to remark that 1 is the first iron complex which shows catalytic activity in the hydrogen-transfer reduction of ketones.

Substrates containing C=C bonds are poorly affected in hydrogen-transfer conditions in the presence of 1, even when the olefin is conjugated with an electron-withdrawing group (see entries 13–16).

Aldehydes are not reduced by 1, 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 $[(PP_3)Fe(O_2CR)]BPh_4$.[12]

Hydrogen-Transfer Reductions Assisted by the Ruthenium(II) Complex 2. The hydrogen-transfer reduction of benzylideneacetone is catalyzed by 2 with high catalytic activity and good chemoselectivity, the largely predominant product being the corresponding unsaturated alcohol; other products formed are the saturated ketone and the saturated alcohol (Table II). The reactions are performed by using either propan-2-ol or cyclopentanol as the hydrogen donor and THF or *p*-dioxane as the solvent. 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. It is also convenient to operate in the presence of a solvent because when the reaction is performed in neat alcohol, the catalytic activity does not increase, while the chemoselectivity decreases due to overreduction to the saturated alcohol.

Other acyclic unsaturated ketones (see Table II) are reduced at the C=C bond with formation of the saturated ketone; further reduction to the saturated alcohol generally takes place.

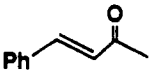
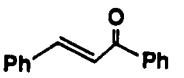
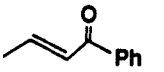
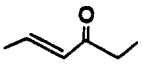
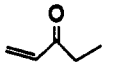
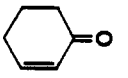
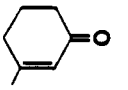
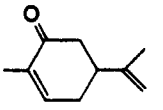
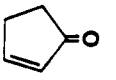
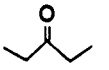
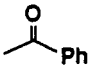
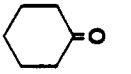
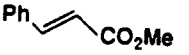
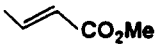
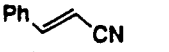
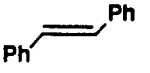
Cyclic enones are reduced at the C=C bond and subsequently to the saturated alcohol when no substituent is present on the olefin group. In the case of hindered C=C bonds (entries 7 and 8), preferential reduction to the unsaturated alcohol takes place.

Unlike the Fe complex, 2 exhibits a good catalytic activity also in the reduction of simple ketones to the corresponding alcohols (entries 10–12).

Substrates bearing a C=C bond conjugated to an electron-withdrawing group are reduced, albeit with a lower catalytic activity as compared to ketone reduction. An exception is represented by cinnamonitrile (entry 15) which is not reduced, probably due to irreversible coordination of the cyano group to the metal (as a matter of fact, acetonitrile reacts with 2 to give the stable complex $[(PP_3)Ru(H)(CH_3CN)]BPh_4$).[3] Simple olefins (entries 16 and 17) are not reduced in the presence of 2.

Aldehydes such as benzaldehyde and cinnamaldehyde are not reduced, and they appear to react irreversibly with the ruthenium catalyst, as one may infer by observing no ketone reduction (ketone = acetophenone or benzylideneacetone) when an aldehyde is present in the reaction mixture. In fact, 2 is known to react with aldehydes to give ethers (RCH_2OCH_2R) and the stable Ru(II) carboxylato complexes of the formula $[(PP_3)Ru(O_2CR)]BPh_4$.[13]

Table II. Hydrogen-Transfer Reduction Catalyzed by $[(PP_3)RuH(H_2)]BPh_4$ (2)[a]

entry	substrate	% conv (time, h)	% sat. ketone	% sat. alcohol	% unsat alcohol
1[b]		85 (2)	5	6	74
2		97 (2)	18	79	0
3		20 (1)	20	0	0
4		58 (3)	56	2	0
5		75 (4)	3	72	0
6		95 (1)	8	83	4
7		55 (5)	0	24[c]	31
8		11 (7)	0	0	11
9		97 (3)	47	50	0
10		97 (1)		97	
11		96 (5)		96	
12		100 (1)		100	
13		75 (7)[d]			
14		48 (7)[e]			
15		0 (7)			
16		0 (7)			
17		0 (7)			

[a] Reaction conditions: [2] = 2×10^{-4} M; [substrate]/[2] = 250; hydrogen-donor = propan-2-ol; [hydrogen-donor]/[substrate] = 50; solvent = THF; T = 60 °C. [b] 40 °C. [c] 16% trans + 8% cis. [d] Reaction product $Ph(CH_2)_2CO_2Me$. [e] Reaction product $CH_3(CH_2)_2CO_2Me$.

(11) Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: London, 1986.
(12) To be published. See ref 13.

Also keto esters such as MeCOCOOMe and $MeCO(CH_2)_2COOEt$ are not reduced by the Ru catalytic system.

We have investigated in some detail the effect of the experimental conditions on the catalytic activity of **2** in the reduction of benzylideneacetone. As already mentioned, the hydrogen donor can be propan-2-ol or cyclopentanol, each of them offering some disadvantages. Propan-2-ol is dehydrogenated in the course of the reaction to give acetone which, like acyclic ketones, has recently been found to react with **2** in a disproportionation reaction, resulting in slow, irreversible deactivation of the catalyst.[13] Such a deactivation is a minor disadvantage when the substrate reduction is fast, whereas in experiments where **2** is less active, deactivation of the catalyst can be competitive with substrate reduction and, therefore, no complete conversion is obtained. In contrast, cyclopentanone, the oxidation product of cyclopentanol, does not poison the Ru catalyst; on the other hand, the ketone which forms is not volatile (as is acetone) and may compete with the substrate for coordination to ruthenium in the course of the catalysis cycle.

The ruthenium catalyst system is very robust; a number of subsequent 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 after each run (*vide infra*). Finally, it is worth mentioning that no other ruthenium complex has been reported so far to selectively catalyze the hydrogen-transfer reduction of α,β-unsaturated ketones to allylic alcohols.

Hydrogen-Transfer Reductions Assisted by the Osmium(II) Complex 3. Hydrogen-transfer reactions catalyzed by the Os(II) complex **3** must be performed in pure donor because the presence of a cyclic ether (THF, *p*-dioxane) inhibits the catalytic activity. Both propan-2-ol and cyclopentanol behave as suitable hydrogen donors, the reactions being generally slightly faster in the case of propan-2-ol, probably due to the lower inhibiting effect of acetone, as compared to cyclopentanone that can readily be evaporated under the reaction conditions (80 °C). Like ruthenium, the osmium catalyst is very stable and several catalytic cycles are accomplished provided the system is recharged with the substrate and the hydrogen donor. The activity is generally lower than with ruthenium, as expected for a 5d metal.

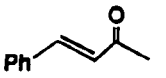
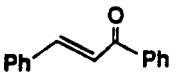
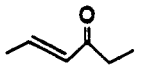
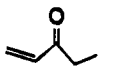
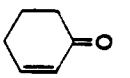
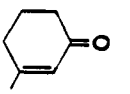
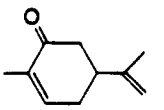
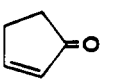
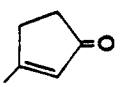
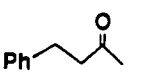
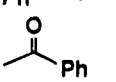
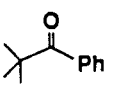
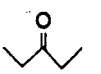
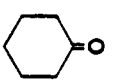
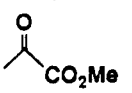
Acyclic α,β-unsaturated ketones are reduced with good catalytic activity to give the corresponding saturated ketones, which are subsequently reduced to saturated alcohols (see entries 1–4 in Table III).

Cyclic α,β-unsaturated ketones are also reduced, but in this case the product distribution is a function of both ring size and steric hindrance about the reducible groups. Cyclohexenone gives a mixture of C=C and C=O reduction products, whereas when the C=C bond is hindered (see entries 6 and 7), the unsaturated alcohol is preferentially formed. In the case of five-membered rings, the main products are the saturated ketones (entries 8 and 9).

Interestingly, the reduction of aldehydes is successfully performed in the presence of the osmium catalyst (Table IV, entries 16 and 17); this behavior is markedly different from those of the Fe and Ru analogues, whose catalytic activity is totally depressed in the presence of aldehydes.

(13) Bianchini, C.; Farnetti, E.; Frediani, P.; Graziani, M.; Peruzzini, M.; Polo, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1336.

Table III. Hydrogen-Transfer Reduction of Ketones Catalyzed by $[(PP_3)OsH(H_2)]BPh_4$ (3)[a]

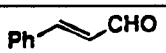
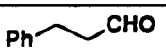
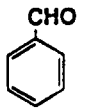
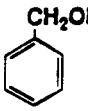
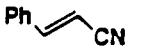
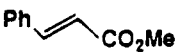
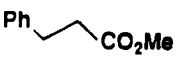
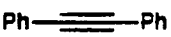
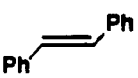
entry	substrate	% conv (time, h)	% sat. ketone	% sat. alcohol	% unsat alcohol
1		91 (3)	72	10	9
2		93 (7)	64	29	0
3		11 (7)	11	0	0
4		100 (8)	95	5	0
5		91 (3)	9	77	5
6		43 (7)	0	6	37
7		2 (7)	0	0	2
8		98 (1)	84	14	0
9		2 (7)	2	0	0
10		75 (7)	7	75	
11		42 (8)		42	
12		2 (7)		2	
13		33 (7)		33	
14		100 (4)		100	
15		1 (5)		1	

[a] Reaction conditions: $[3] = 2 \times 10^{-4}$ M; [substrate]/[3] = 250; solvent and hydrogen-donor = propan-2-ol; T = 80 °C.

As for the reduction of olefin groups, we observe no catalytic activity of **3** with either simple olefins or olefins activated by electron-withdrawing groups; only in the case of methyl cinnamate (entry 19) are traces of the reduction product detected.

The triple bond of diphenylacetylene (entry 23) is reduced to the double bond, no further reduction being observed. The incapability of catalyzing the reduction of C=C bonds is not due to irreversible coordination of the olefin to the metal, as shown by experiments performed using a mixture of a ketone (unsaturated or saturated) and an olefin: the ketone is regularly reduced to the expected product (or mixture of products) with no loss of activity due to the presence of the olefin.

Table IV. Hydrogen-Transfer Reduction of Other Substrates Catalyzed by $[(PP_3)OsH(H_2)]BPh_4$ (3)

entry	substrate	% conv (time, h)	products (%)			
16		45 (3)		(9)		(36)
17		99 (3)		(99)		
18		0 (7)				
19		3 (7)		(3)		
20		0 (7)				
21		5 (7)		(1)		(4)
22		0 (7)				
23		68 (6)		(65)		(3)

[a] Reaction conditions: see Table III.

In view of the results obtained, one is surprised to notice that α,β-unsaturated ketones are reduced to the saturated ketone (apparent C=C reduction), whereas simple olefins (even when activated by electron-withdrawing groups other than carbonyl) are not reduced, and simple ketones are readily reduced.

A number of experiments were performed using substituted allylic alcohols as substrates in order to ascertain whether an isomerization process was operative. The unsaturated alcohol Ph—CH=CHCH(OH)Me (reduction product of benzylideneacetone) is slowly isomerized to the saturated ketone in *p*-dioxane or THF as solvent, whereas in an alcohol such as propan-1-ol (primary alcohol, poor hydrogen-donor) the isomerization is much faster. After 7 h, the product distribution is as follows: 23% of the unsaturated alcohol, 51% of the the saturated ketone (isomerization product), 26% of the saturated alcohol (reduction product).

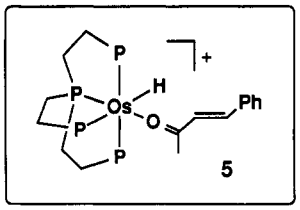
Substitution of the dinitrogen derivative $[(PP_3)Os(H)(N_2)]BPh_4$ (4) for 3 results in an increase of the catalytic activity, the allylic alcohol being rapidly and selectively isomerized to the saturated ketone (1,2-dichloroethane, argon atmosphere, 80 °C). The higher activity of the dinitrogen adduct 4 as compared to 3 is reasonably due to the greater lability of the N_2 ligand *vs* H_2[4] and thus to a higher concentration of the $[(PP_3)OsH]^+$ fragment in the reaction mixture (*vide infra*). In conclusion, the reduction of α,β-unsaturated carbonyl compounds catalyzed by 3 does occur *via* initial C=O group reduction, with subsequent fast isomerization to the saturated ketone.

In this respect, it is worth mentioning that 4 (and therefore the unsaturated system $[(PP_3)OsH]^+$, *vide infra*) is capable of catalyzing cis–trans isomerization of simple olefins, as shown by the reaction with *cis*-stilbene which is rapidly converted to *trans*-stilbene in refluxing THF.

NMR Studies on the Catalytic Reduction of Benzylideneacetone. $^{31}P\{^1H\}$ NMR studies were carried out on Fe- and Ru-assisted reductions of benzylideneacetone resembling as closely as possible the catalytic reactions described in the previous sections. Actually, slightly different concentrations of the various reagents, particularly the catalyst to substrate ratio, were used in order to obtain ^{31}P NMR spectra with a reasonable signal to noise ratio. These were recorded on solution samples withdrawn after reaction times sufficiently long to give appreciable conversion of benzylideneacetone to its reduction products (3 and 1 h for Fe and Ru, respectively). Valuable information was obtained after quenching the reactions with nitrogen or carbon monoxide. The ^{31}P NMR spectra showed that (i) the iron complex 1 had only partially converted to either $[(PP_3)Fe(H)(N_2)]BPh_4$ or $[(PP_3)Fe(H)(CO)]BPh_4$ (*ca.* 40%)[2] and (ii) appreciable decomposition to undefined iron compounds had occurred (*ca.* 30%). Both these findings are nicely consistent with the minor activity and stability observed for the iron catalyst as compared to ruthenium. As a matter of fact, in the Ru-assisted reaction, the spectra unambiguously showed that all the starting metal complex had disappeared. In particular, all ruthenium was incorporated into the corresponding dinitrogen or CO derivatives $[(PP_3)Ru(H)(N_2)]BPh_4$ and $[(PP_3)Ru(H)(CO)]BPh_4$, respectively.[3]

Analogous experiments could not be done for the osmium complex 3 which is not sufficiently soluble in pure propan-2-ol, where the catalytic reactions are performed, to obtain informative ^{31}P NMR spectra. Therefore, in order to gain insight into the Os catalysis system, we decided to attempt a different approach.

To a CD_2Cl_2 solution of the η^1-dinitrogen derivative 4, a stoichiometric amount of benzylideneacetone was added under an argon atmosphere, and the resulting solution was transferred into an NMR tube. $^{31}P\{^1H\}$ and ^1H NMR spectra were immediately recorded, which showed an almost quantitative conversion of 4 to a new Os complex (from now on 5) exhibiting a ^{31}P AMQ_2 spin system (typical of octahedral PP_3 metal complexes)[2-4] and containing a



$^{31}P\{^1H\}$ NMR: AMQ_2 spin system

δP_A 105.39, δP_M 24.10, δP_Q 30.36

$J(P_AP_M)$ 12.3, $J(P_AP_Q)$ 4.9, $J(P_MP_Q)$ 6.0 Hz

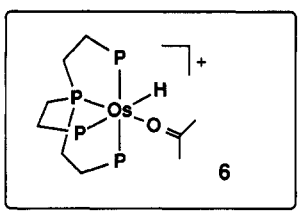
^1H NMR: $\delta_{Os\text{-}H}$ -7.22 dtd

$J(HP_M)$ 72.6, $J(HP_Q)$ 26.0, $J(HP_A)$ 11.8 Hz

δ(MeCO) 2.37 s

δ(CH=CH) 7.40 d; 6.74 d

J(HH) 16.3 Hz



$^{31}P\{^1H\}$ NMR: AMQ_2 spin system

δP_A 106.10, δP_M 25.40, δP_Q 31.45

$J(P_AP_M)$ 13.1, $J(P_AP_Q)$ 5.5, $J(P_MP_Q)$ 6.5 Hz

^1H NMR: $\delta_{Os\text{-}H}$ -7.07 dtd

$J(HP_M)$ 72.0, $J(HP_Q)$ 26.1, $J(HP_A)$ 12.1 Hz

$\delta(Me_2CO)$ 1.84 s

Figure 1. Sketches and relevant NMR data for complexes **5** and **6**.

terminal hydride ligand (dtd at −7.22 ppm). Most importantly, the ^1H NMR spectrum showed an AB pattern in the olefin hydrogen region quite similar to that exhibited by free benzylideneacetone in the same solvent, but slightly low-field shifted. Addition of a 2-fold excess of propan-2-ol *via* syringe resulted in quantitative formation of free $PhCH_2CH_2COMe$ and of the known η^1-*O*-acetone complex $[(PP_3)Os(H)(\eta^1\text{-}OCMe_2)]BPh_4$ (**6**) [ν(Os—O=CMe_2) = 1652 cm^{-1}].[4,14] From a comparison of the spectroscopic properties of **5** and **6** (Figure 1), one may readily conclude that the two compounds share the same primary geometry in which the Os center is octahedrally coordinated by the four phosphorus atoms of PP_3, by a terminal hydride ligand, and by a ketone molecule bound through the oxygen atom. Substitution of THF-d_8 for CD_2Cl_2 as the solvent of the NMR experiments has a dramatic effect, since THF prevails over benzylideneacetone in coordinating the metal center once N_2 has been eliminated. As a result, the known THF adduct $[(PP_3)Os(H)(THF)]^+$ forms.[4] This finding is consistent with the poor catalytic activity shown by **3** when the hydrogen-transfer reactions are carried out in THF or *p*-dioxane solutions. As reported above, such a solvent effect is not observed for Fe and Ru and, in fact, the corresponding $[(PP_3)MH]^+$ fragments are not able to form stable adducts with either THF or *p*-dioxane.

Interestingly, isolated **6** in CH_2Cl_2 exchanges the acetone ligand with benzylideneacetone when an excess of the latter ketone is added, as shown by the fact that subsequent addition of propan-2-ol results in formation of free $PhCH_2CH_2COMe$ (GC).

Finally, in a separate experiment, a 10-fold excess of PhCH=CHCH(OH)Me was added to a CD_2Cl_2 solution of **6** under argon at 30 °C. A reaction occurred to give quantitative conversion of the unsaturated alcohol to the saturated ketone after 3 h (^1H NMR, GC). Upon CO bubbling into the NMR tube, the $^{31}P\{^1H\}$ NMR spectrum showed formation of $[(PP_3)Os(H)(CO)]BPh_4$.[4]

Attempts to trap Fe or Ru η^1-*O*-benzylideneacetone adducts similar to **5** by reacting the corresponding dinitrogen derivatives with the unsaturated ketone were unsuccessful, although reactions did take place to give the allylic alcohol upon subsequent addition of propan-2-ol. Such a result is not completely unexpected since osmium forms rather kinetically inert complexes. For this reason, Os is often used to trap reactive species not isolable with the use of its 3d and 4d congeners.

Some Considerations on the Hydrogen-Transfer Reduction of Benzylideneacetone. Before we report our conclusions on the catalysis cycles, it may be convenient to spend a few words on the stability of complexes **1–3**. Reactivity studies have clearly shown that the solution chemistry of these nonclassical trihydrides is dominated by the different metal–dihydrogen bond strengths, which increase in the order Ru ≪ Fe ≤ Os.[2-4,15]

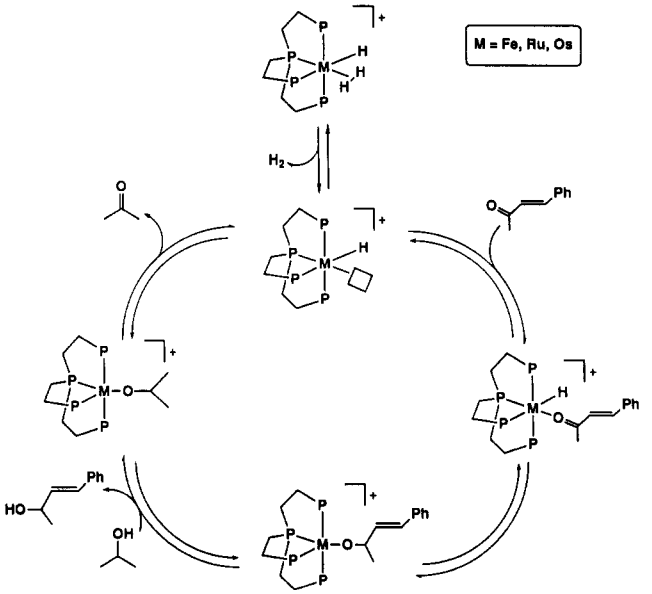
Displacement of the dihydrogen molecule by other neutral ligands such as N_2, CH_3CN, PR_3, or CO to give $[(PP_3)M(H)(L)]^+$ derivatives is a feasible reaction for all compounds; however, more drastic conditions are generally required for Fe and Os than for Ru.[2-4] Regardless of the metal center, ligand substitution reactions are not carried out in solutions degassed with nitrogen or dihydrogen where **1–3** and the η^1-dinitrogen derivatives $[(PP_3)M(H)(N_2)]^+$ are indefinitely stable. From this observation, one may readily realize why the catalytic activity of **1–3** is almost totally depressed in the presence of H_2 or N_2, which evidently compete with the ketonic substrates in coordination to the metal center.

In light of the NMR evidence reported above, there is little doubt that **1–3** are catalyst precursors for the hydrogen-transfer reduction of benzylideneacetone, the real catalysts 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, it is reasonable to think that also iron and ruthenium initially coordinate the unsaturated ketone *via* the oxygen atom in a cis position to the terminal hydride ligand.

(14) Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034.

(15) Eckert, J.; Albinati, A.; White, R. P.; Bianchini, C.; Peruzzini, M. *Inorg. Chem.* **1992**, *31*, 4241.

Scheme I



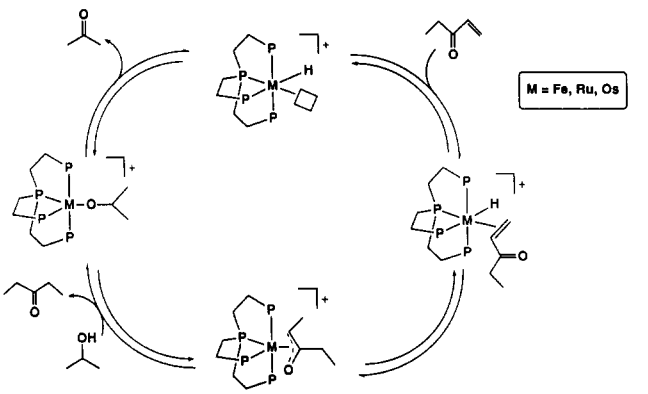
Provided this initial step occurs for all metals, a common catalysis cycle can be proposed, which is illustrated in Scheme I. This involves migration of hydride from metal to coordinated ketone to give an alkoxy complex. Reaction of the latter species with the hydrogen donor (e.g. propan-2-ol) cleaves the M–O bond with consequent formation of free allylic alcohol and an isopropoxy complex. Finally, the unsaturated hydride is regenerated *via* a β-H elimination reaction, thereby closing the catalysis cycle.

Catalytic cycles of the type shown in Scheme I are well-known and experimental evidence of each single step[1h,16,17] has been provided except for η^1-*O*-coordination of the α,β-unsaturated ketone reported in this paper.

The migration of hydride from metal to the ketonic carbon atom is generally considered the rate determining step, which is consistent with our NMR evidence for the Os system. The migration may be viewed as a concerted process involving a four-centered intermediate or transition state; thus it has been suggested that an η^2-*C,O*-ketone bonding mode would favor the insertion reaction.[17] Although we have no evidence of a change from η^1-*O*- to η^2-*C,O*-coordination of benzylideneacetone, one cannot exclude *a priori* that such a shift may occur in our system too. On the other hand, migrations of hydrides to C_β-atoms of σ-bonded ligands are also well-known.[18] In our opinion, the remarkable steric hindrance of the metal center in PP_3 complexes suggests the preservation of the η^1-*O*-bonding mode in the hydride migration process.

It is worth mentioning that a number of metal-catalyzed hydrogen-transfer (and hydrogenation as well) reductions of α,β-unsaturated ketones have been suggested to proceed *via* π-oxaallyl intermediates.[1e,l] We exclude this mechanism in the reduction of benzylideneacetone for several reasons. First, the intermediacy of π-oxaallyl complexes requires π-coordination of the double bond of the ketone prior to hydride migration, which contrasts with our observation of an Os η^1-*O*-benzylideneacetone intermediate. Second, the $[(PP_3)MH]^+$ fragments (M = Fe, Ru) are not capable for steric reasons to coordinate alkenes bearing bulky substituents such as styrene, a feature that makes these systems excellent catalysts for the selective hydrogenation of 1-alkynes to alkenes.[6,7] Finally, the mechanisms involving π-oxaallyl intermediates generally lead to the selective hydrogenation of the double bond of α,β-unsaturated ketones, which contrasts with the selectivity shown by the PP_3 complexes.[1e,l]

Scheme II



In light of all these considerations, however, a reaction path occurring *via* a π-oxaallyl intermediate (Scheme II) well accounts for the different chemoselectivity observed in the **1**–**3**-catalyzed reduction of less hindered α,β-unsaturated ketones such as vinyl ethyl ketone, which is converted to diethyl ketone (this is subsequently reduced to pentan-3-ol in the case of Ru). Consistent with the steric properties of the substrate, 2-cyclohexen-2-one (but not its 3-methyl derivative which is selectively converted to the unsaturated alcohol) might be reduced at iron *via* two *independent reaction pathways*, one of the type shown in Scheme I, the other of the type shown in Scheme II. In fact, the starting ketone is reduced at both unsaturated functionalities with formation of both cyclohexanone, which is subsequently reduced to cyclohexanol, and 2-cyclohexen-1-ol, which is stable under the hydrogen-transfer conditions.

Isomerization of PhCH=CHCH(OH)Me Catalyzed by 3. Of the three catalysts investigated in this paper, only the $[(PP_3)OsH]^+$ fragment has been found capable of isomerizing the rearrangement of allylic alcohols to the corresponding saturated ketones. As above reported, the isomerization of PhCH=CHCH(OH)Me is catalyzed by **3** or **4** with no need of coreactants. The reaction is best performed in noncoordinating solvents under an argon atmosphere. When alcoholic solvents are employed, subsequent reduction to saturated alcohol may take place.

A number of intramolecular hydrogen-transfer reactions leading to the formal disproportionation of allylic alcohols to saturated ketones are known.[19] Distinct mechanisms have been proposed depending on the nature of the metal catalyst. When the latter does not contain hydride ligands, the reactions are believed to occur *via* π-oxaallyl intermediates formed upon β-H abstraction from CH(OH)R groups.[20] This step is not easily accessible to our Os system, which already contains a terminal hydride. Accordingly, we suggest the alternative, well-known mechanism illus-

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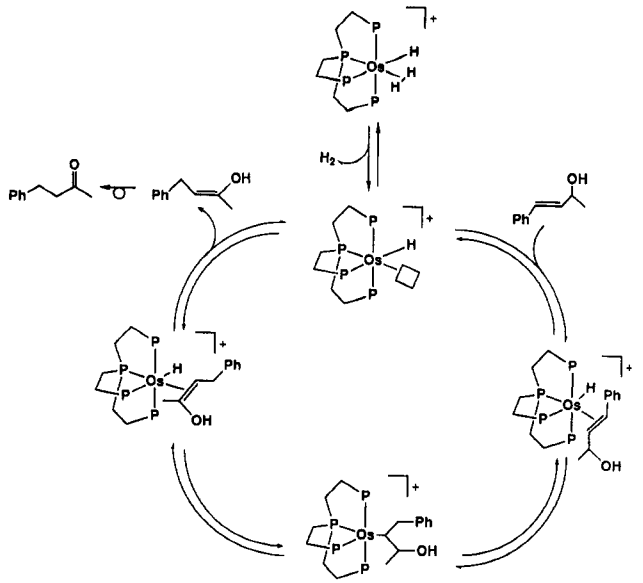
(17) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 1159.
(18) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.
(19) Bäckvall, J.-E.; Chowdhuri, R. L.; Karlsson, U.; Wang, G. In *Perspectives of Coordination Chemistry*; Williams, A., Floriani, C., Merbach, A., Eds.; VCH: Basel, 1992; p 463.
(20) Alper, H.; Hachem, K. *J. Org. Chem.* **1980**, *45*, 2269.

Scheme III



trated in Scheme III.[21] This involves coordination of the allylic alcohol to Os *via* the double bond, followed by hydride migration to the =CH(Ph) carbon atom. As a result, a σ-alkyl ligand forms, which is appropriate to generate both hydride and $PhCH_2CH{=}C(OH)Me$ through a β-H elimination step. On displacement from the metal, the olefin rapidly converts from the enol form to the saturated ketone.

Indirect support to the hydride migration/β-H elimination pathway is provided by the effectiveness of $[(PP_3)OsH]^+$ to catalyze the isomerization of *cis*-stilbene to *trans*-stilbene.

The incapability of Fe and Ru of catalyzing the isomerization of allylic alcohols is attributed to their incapability of coordinating substituted double bonds,[2,3] unless the double bond is conjugated with an ester group (entry 14 for Fe, entries 13 and 14 for Ru). Actually, the presence of an ester substituent at the double bond makes the electronic and structural situation of the olefin comparable with that of α,β-unsaturated ketones, and therefore, the reduction of these olefins may reasonably proceed *via* π-oxaallyl intermediates (Scheme II).

Concluding Remarks

The nonclassical trihydrides **1–3** are efficient catalyst precursors for the reduction of α,β-unsaturated ketones *via* hydrogen-transfer from secondary alcohols. They combine high activity and selectivity under mild reaction conditions with ease of preparation, handling, and particularly for Ru and Os, recycling.

Irrespective of the metal center, the overall steric and electronic situation in the coordination sphere of all catalysts $[(PP_3)MH]^+$ appears as appropriately designed to favor the reduction of the carbonyl group of α,β-unsaturated ketones bearing bulky substituents at the C=C double bond. In theory, this is also valid for Os, the observed selectivity in saturated ketone being due to a subsequent isomerization reaction. On the other hand, the reduction of the C=C bond is observed when either the latter is not sterically hindered or the C=O carbon atom bears a bulky substituent. Other olefins are not reduced by our catalytic systems, with the exception of α,β-unsaturated esters whose structural and electronic features are similar to those of conjugated enones.

A remarkable reaction is represented by the reduction of mixtures of saturated and unsaturated ketones in the presence of the iron catalyst as we note a high substrate selectivity toward unsaturated ketones.

A vacant coordination site for the incoming ketone is provided by H_2 unfastening from the starting complexes. This process does not take place with the same ease for all η^2-H_2 precursors as they exhibit different metal to dihydrogen bond strengths, which increase in the order $Ru \ll Fe \leq Os$.[3,5,15] It is a rapid preequilibrium between the nonclassical trihydrides and the monohydrides which determines the concentration of the catalytically active species. In the case of Ru, the equilibrium is shifted toward the monohydride $[(PP_3)RuH]^+$, whereas for Fe and Os, part of the metal is actually "waiting" as $M(H)(H_2)$.

With the use of the 5d metal, we have been able to show that benzylideneacetone occupies the free coordination site *via* the ketonic oxygen (η^1-*O*-bonding mode).

Finally, we wish to highlight the fact that for the metals in the iron triad, not only ruthenium and osmium but also iron can form complexes capable of acting as good catalysts for the selective reduction of unsaturated organic substrates. This opens a rather promising and largely unexplored area of research.

Acknowledgment. Thanks are due to Progetti Finalizzati "Chimica Fine II", CNR, Rome, Italy, and to the EC Programme "Human Capital and Mobility-Networks".

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