SELECTIVE HYDROGENATION OF BENZYLIDENEACETONE CATALYZED BY IRIDIUM DIPHOSPHINE COMPLEXES

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(Received March 14, 1988; accepted July 5, 1988)

Summary

Hydrogenation of benzylideneacetone ($PhCH{=}CHCOCH_3$) is catalysed by iridium diphosphine complexes of the type $[Ir(P{-}P)_2]^+$ (P—P = dpe, dpp, dpb, (*S*, *S*)-chiraphos, (*R*)-prophos,, (+)-diop and (*S*)-prolophos) and by systems formed *in situ* from $[Ir(cod)Cl]_2$ or $[Ir(cod)(OCH_3)]_2$ (cod = 1,5-cyclooctadiene) and diphosphines.

1-Phenyl-1-buten-3-ol [$PhCH{=}CHCH(OH)CH_3$] is selectively produced in high yields using $[Ir(P{-}P)_2]^+$ (P—P = diop, prolophos) as catalyst precursor or high P/Ir ratios in the systems prepared *in situ*. Optical yields up to 30% in the *S*(—)-unsaturated alcohol are obtained with chiral diphosphines as ligands. Catalytic results are given together with spectroscopic data and some equilibria are proposed to account for the different activities and selectivities observed in the hydrogenation. The length of the carbon atom chain in the diphosphine seems to play a crucial role in determining the distribution of products.

Introduction

The asymmetric hydrogenation of prochiral organic substrates has received considerable attention over the last decade, particularly the reduction of aminoacid precursors catalysed by rhodium phosphine complexes, and several reviews are available in the literature [1]. Optically active alcohols have been obtained by asymmetric hydrogenation of ketones with molecular hydrogen and in hydrosilylation [1], or using alcohols and base as reducing agents [2]. Selective reduction of the carbonyl group in the presence of olefinic double bonds has been achieved in a few cases [3]. When the two functions are conjugated, the selective reduction of the C=O bond

0304-5102/89/$3.50

is more difficult; nevertheless α, β-unsaturated aldehydes are successfully reduced to the corresponding unsaturated alcohols by some systems [4].

We recently reported the first highly selective hydrogenation of the carbonyl group in the α,β-unsaturated ketone $C_6H_5CHCHCOCH_3$ (benzylideneacetone) using iridium systems with monophosphines as catalysts [5]. These results prompted us to investigate the same reaction in the presence of optically active diphosphine iridium complexes, in the attempt to combine chemo- and enantioselectivity to obtain the optically active unsaturated alcohol from the unsaturated ketone.

In the present work, catalytic results together with spectroscopic data are discussed and interpreted with the aim of identifying the species present in solution in our experimental conditions.

Experimental section

Chemicals

Benzylideneacetone (Fluka) was recrystallized three times from propan-2-ol before use. Toluene (Carlo Erba RPE-ACS) was distilled before use. Diphosphines were purchased from Strem Chemicals, except prolophos [6].

dpe = 1,2-bis(diphenylphosphino)ethane; dpp = 1,3-bis(diphenylphosphino)propane; dpb = 1,4-bis(diphenylphosphino)butane; (*S*, *S*)-chiraphos = (—)-(2*S*, 3*S*)-bis(diphenylphosphino)butane; (*R*)-prophos = (*R*)-(+)-1,2-bis(diphenylphosphino)propane; (+)-diop = (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4bis(diphenylphosphino)butane; (*S*)-prolophos = (*S*)-(—)-*N*-(diphenylphosphino)-2-diphenylphosphinooxymethylpyrrolidine.

NMR spectra were recorded on a Bruker WP 80 instrument. Chemical shifts are referred to TMS (^1H) and 85% H_3PO_4 (downfield positive) (^{31}P).

Syntheses

All syntheses were effected in a nitrogen atmosphere using standard Schlenk-tube techniques. $[Ir(cod)Cl]_2$, $[Ir(cot)_2Cl]_2$ and $[Ir(cod)(OCH_3)]_2$ (cod = 1,5-cyclooctadiene, cot = cyclooctene) were prepared according to the literature [7, 8]. $[Ir(dpe)_2]BPh_4$, $[Ir(dpp)_2]BPh_4$, $[Ir(dpb)_2]BPh_4$, $[Ir(chiraphos)_2]BPh_4$, $[Ir(prophos)_2]BPh_4$, $[Ir(diop)_2]BPh_4$ were synthesized by slight modifications of standard literature procedures [9, 10].

Preparation of $[Ir(prolophos)_2]BPh_4$

140 mg $[Ir(cot)_2Cl]_2$ (0.156 mmol) were added to 370 mg (*S*)-prolophos (0.786 mmol) dissolved in 10 ml distilled THF. Excess $NaBPh_4$ (300 mg, 0.9 mmol) was then added, and the resulting dark red solution was evaporated to dryness. The residue was taken up in 5 ml CH_2Cl_2 and the sodium salts filtered off under nitrogen. Finally, 10 ml CH_3OH were added, the CH_2Cl_2 was evaporated and the volume of the solution reduced to 5 ml *in vacuo*. The red-orange precipitate was filtered, washed twice with diethyl ether and dried. Yield 80%.

Anal. Found: C 67.7, H 5.52, N 1.90%; calcd. for $C_{82}H_{78}BN_2O_2P_4Ir$: C 67.9, H 5.42, N 1.93%.

^{31}P NMR ($CDCl_3$, 223 K): δ 115.1 (t), 55.0 (t), δ 101.4 (t), 58.9 (t), J(P—P) = 28 Hz, and δ 83.8, 72.8 (multiplets) in the ratio 13:1.2:1. The two series of triplets were assigned to *cis*- and *trans*-[Ir(prolophos)$_2$]BPh_4. At 300 K, the ^{31}P NMR spectrum consisted of three series of broad, structureless bands. The intensity of the minor triplets increased with the temperature, reaching about half that of the major bands at room temperature.

Hydrogenation reactions

All reactions were carried out in a stainless steel autoclave with magnetic stirring. In a typical experiment, 0.02 mmol of catalyst were dissolved in 50 ml of deaerated toluene and kept in H_2 flow for 15 min, then 10 mmol of benzylideneacetone were added and the resulting solution transferred into the autoclave under hydrogen. The pressure was brought to 20 atm and the system heated to 100 °C. Samples were taken and analyzed by GLC on a Perkin Elmer Sigma 3B gas chromatograph equipped with a thermal conductivity detector, using helium as carrier gas and a 25 m Supelcowax 10 wide-bore capillary column.

At the end of reaction, the composition of the mixture of products was determined by GLC on the distillate, and optical rotations were measured using a Perkin Elmer 141 polarimeter. Optical purities were calculated on the basis of the value $[\alpha]_D^{20} = 24.7°$ (*c* 5, $CHCl_3$) [11] for the optically pure 1-phenyl-1-buten-3-ol.

Results

Hydrogenation of benzylideneacetone

In Tables 1 and 2 are reported the results obtained in the asymmetric hydrogenation of benzylideneacetone catalyzed by the system formed *in situ* from [Ir(cod)$(OCH_3)]_2$ and diphosphine and by $[Ir(P—P)_2]^+$ respectively.

From Table 1 the general trend shown is that the selectivity in unsaturated alcohol increases with the diphosphine/Ir ratio: at high (P—P)/Ir values all the systems tested are highly selective towards reduction of the carbonyl group (Table 1, runs 4, 7, 10, 13). At (P—P)/Ir < 2, on the contrary, the saturated ketone together with some saturated alcohol are formed (see run 1, Table 1 as an example). The catalytic activity is not dramatically affected by the presence of an excess of diphosphine, although it generally decreases when (P—P)/Ir ratios > 2 are used. The selectivity of the system changes to some extent in the initial period of reaction, especially at intermediate (P—P)/Ir ratios, until it reaches its final value (see run 9, Table 1 as an example). The highest optical purity is obtained with prolophos as ligand (30% e.e., run 13, Table 1).

TABLE 1

Asymmetric hydrogenation of benzylideneacetone (BDA) catalyzed by $[Ir(cod)(OMe)]_2$ + P—P[a]

	P—P	(P—P)/Ir	Time (h)	BDA (%)	A (%)	B (%)	C (%)	Sel.[b] (%)	$\alpha_{exp.}$	(c, $CHCl_3$)[c]	Opt. purity[d] (%)	
1	chiraphos	1	5	1	73	26	0	0	—	—	—	
2		2	20	0	4	93	3	3	—	—	—	
3		5	21	10	4	14	72	80	−0.032	(4.966)	—	
4		10	27	9	2	5	84	92	−0.080	(4.131)	7.8	[*S*(−)]
5	prophos	2	5	6	5	41	48	51	0		—	
6		5	23	3	0	7	90	93	+0.121	(5.073)	9.6	[*R*(+)]
7		10	23	11	1	4	84	94	+0.132	(5.296)	10.1	[*R*(+)]
8	diop	2	27	2	3	45	50	51	−0.025	(3.705)	—	
9		5	7	64	14	3	19	53				
			30	4	5	13	78	81	−0.305	(6.460)	—	
10		10	89	12	2	2	84	95	−0.210	(4.780)	17.8	[*S*(−)]
11	prolophos	2	23	1	3	44	52	52	−0.200	(4.046)	—	
12		5	90	1	3	18	78	79	−0.350	(4.709)	—	
13		10	95	3	2	3	92	95	−0.350	(4.710)	30.1	[*S*(−)]

[a]Reaction conditions: solvent toluene, $[Ir] = 4 \times 10^{-4}$ M, $T = 100$ °C, $pH_2 = 20$ atm, sub/cat = 500; A = sat. ketone; B = sat. alcohol; C = unsat. alcohol.

[b]Selectivity: (% unsat. alcohol/% conversion) × 100.

[c]c = g per 100 cc soln.

[d]See Experimental section.

TABLE 2

Asymmetric hydrogenation of benzylideneacetone (BDA) catalyzed by $[Ir(P—P)_2]^{+a}$

	Precursor	(P—P)add./Ir	Time (h)	BDA (%)	A (%)	B (%)	C (%)	Sel.[b] (%)	$\alpha_{exp.}$	(c, $CHCl_3$)[c]	Opt. purity[d] (%)	
1	$[Ir(chiraphos)_2]^+$	—	28	2	70	28	0	0	—	—	—	
2		3	20	100	0	0	0	—	—	—	—	
3		8	90	97	1	0	2	—	—	—	—	
4	$[Ir(prophos)_2]^+$	—	48	9	80	9	2	2	—	—	—	
5		8	66	99	1	0	0	—	—	—	—	
6	$[Ir(diop)_2]^+$	—	114	4	2	5	89	93	−0.220	(5.101)	17.5	[S(−)]
7		8	116	69	2	0	29	93	—	—	—	
8	$[Ir(prolophos)_2]^+$	—	27	3	4	10	83	86	−0.240	(4.394)	—	
9		8	89	3	1	2	94	97	−0.391	(5.088)	31.1	[S(−)]

[a]Reaction conditions as in Table 1; A = sat. ketone; B = sat. alcohol; C = unsat. alcohol.
[b]Selectivity: (% unsat. alcohol/% conversion) ×100.
[c]c = g per 100 cc soln.
[d]See Experimental section.

The data reported in Table 2 concerning cationic complexes $[Ir(P—P)_2]^+$ used as catalyst precursors show opposite selectivities, depending on whether chiraphos and prophos or diop and prolophos are used as ligands (runs 1, 4 and 6, 8). Such a behavior is definitely different from that shown by the systems *in situ* at (P—P)/Ir > 2.

Furthermore, an excess of free diphosphine has a great influence on the catalytic activity in the case of cationic complexes, leading to complete inhibition of the reaction rate for chiraphos and prophos (runs 2, 3 and 5, Table 2). In the case of $[Ir(diop)_2]^+$ and $[Ir(prolophos)_2]^+$, despite a great loss in catalytic activity, the system still catalyzes the selective reduction of benzylideneacetone to the unsaturated alcohol (runs 7, 9, Table 2). $[Ir(prolophos)_2]^+$ gives 31% optical purity in the [*S*(—)] unsaturated alcohol in the presence of excess of diphosphine.

Table 3 reports results obtained in the reduction of benzylideneacetone using non-chiral iridium–diphosphine systems. Selectivity in the unsaturated alcohol is found using $[Ir(dpb)_2]^+$ or systems *in situ* at (P—P)/Ir > 2; the presence of an excess of dpe inhibits the catalytic activity when added to $[Ir(dpe)_2]^+$ (Table 3, run 4).

^1H and ^{31}P NMR results

The reaction of $[Ir(P—P)_2]^+ + H_2$ was investigated via ^1H and ^{31}P NMR in our experimental conditions. $[Ir(diphos)_2]^+$ gives a mixture of *cis*- and *trans*-$[H_2Ir(diphos)_2]$ by reaction with H_2 at room temperature (70 - 80% of *cis* isomer) [10]. There is no noticeable change in the ^{31}P NMR spectrum even after 24 h in toluene under 20 atm of H_2 and at 100 °C.

$[Ir(chiraphos)_2]^+$ gives *cis*-$[H_2Ir(chiraphos)_2]^+$ [10] with H_2 at room temperature (^{31}P in toluene/CH_2Cl_2: δ 32.2 (t), 22.1 (t), J(P—P) = 12.5 Hz), which isomerizes to the *trans* isomer after 3 h at reflux in toluene under H_2 (^{31}P: δ 36.5 (s); ^1H in C_6D_6/CD_2Cl_2: quintet at δ — 10.4, J(P—H) = 14.5 Hz).

The ^1H and ^{31}P NMR spectra of $[Ir(diop)_2]^+ + H_2$, on the other hand, show the presence of the *cis*-dihydride as the only detectable species, both at room temperature and at reflux as above (^{31}P: δ —17.8 (t), —28.9 (t), J(P—P) = 13.0 Hz; ^1H: complex multiplet centered at δ —12.5 ppm, $J(P—H)_{trans}$ = 93.5 Hz). At longer reaction times (24 - 48 h) under 20 atm of H_2 and 100 °C, the ^{31}P NMR spectrum shows the slow formation of other unidentified species. $[Ir(dpb)_2]^+$ shows the same behavior as the diop analogue on treatment with H_2 in refluxing toluene (^1H: complex multiplet centered at δ — 12.56, $J(P—H)_{trans}$ = 112.3 Hz).

$[Ir(prolophos)_2]^+$ gives two different *cis*-dihydrides by reaction with H_2 at room temperature (^{31}P in $CDCl_3$: two major triplets at δ 91.2, 37.7, J(P—P) = 16 Hz, and two minor triplets at δ 68.3, 40.9, J(P—P) = 20 Hz, in the intensity ratio 10:1; ^1H in $CDCl_3$: doublet of triplets centered at δ — 11.0, $J(P—H)_{cis}$ = 14.8 Hz, $J(P—H)_{trans}$ = 111.8 Hz, and doublet of triplets centered at δ — 12.5, $J(P—H)_{cis}$ = 22.4 Hz, $J(P—H)_{trans}$ = 95.8 Hz). On the basis of the NMR spectra, it can be concluded that both dihydrides

TABLE 3

Hydrogenation of benzylideneacetone (BDA) catalyzed by Ir/diphosphine systems[a]

	Catalyst	(P—P)add./Ir	Time (h)	BDA (%)	A (%)	B (%)	C (%)	Sel.[b] (%)
1	$[Ir(dpe)_2]^+$	—	24	—	80	20	—	—
2	$[Ir(dpp)_2]^+$	—	45	19	78	2	1	1
3	$[Ir(dpb)_2]^+$	—	123	61	4	1	34	87
4	$[Ir(dpe)_2]^+$ + dpe	3	24	99	1	0	0	0
5	$[Ir(cod)(OCH_3)]_2$ + dpe	2	2	36	23	22	19	30
			6	1	13	81	5	5
6	$[Ir(cod)(OCH_3)]_2$ + dpe	10	30	93	1	0	6	86
7	$[Ir(cod)(OCH_3)]_2$ + dpb	2	29	5	6	8	81	85
8	$[Ir(cod)(OCH_3)]_2$ + dpb	10	95	62	3	1	34	89

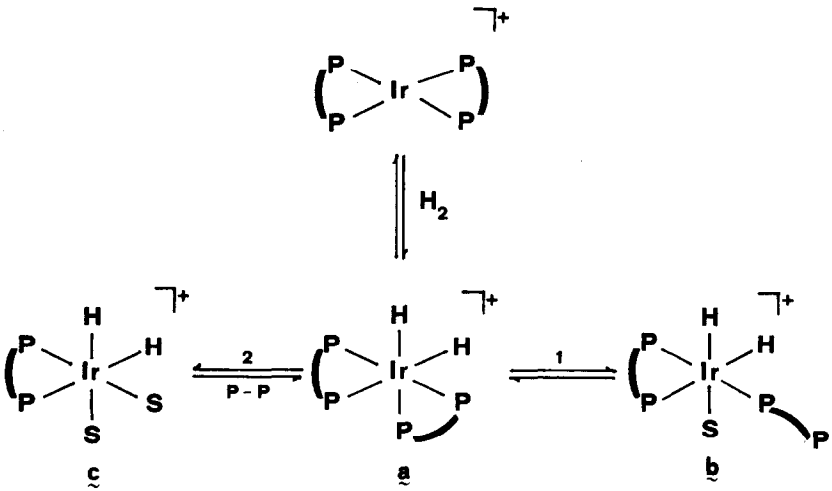
[a]Reaction conditions as in Table 1; A = sat. ketone; B = sat. alcohol; C = unsat. alcohol.
[b]Selectivity: (% unsat. alcohol/% conversion) ×100.

are formed from *trans*-$[Ir(prolophos)_2]^+$. The ^{31}P NMR spectrum remains unchanged by cooling the sample to 223 K.

Discussion

Catalytic results show that the chemical behavior of these iridium–diphosphine complexes is dependent on the steric properties of the ligand used, and in particular on the length of the carbon atom chain of the chelating ring of the diphosphine. Seven-membered rings in metal chelate complexes are known to be flexible [12], and their tendency to give ring-opening dissociation is much higher than that of five-membered rings. $[Rh(dpb)_2]^+$ and $[Rh(diop)_2]^+$ react with H_2 through a mechanism whose kinetics suggest the involvement of intermediates with a diphosphine bound in a monodentate fashion [13]. Also, the formation of species where the ligand is bridging two metal atoms is known to occur with these larger diphosphines [9, 14]. In some cases, complexes with a monodentate diphosphine coordinated to the metal have been isolated and/or characterized [15].

In the case of the iridium–bis(diphosphine) complexes, the formation of similar species can also be suggested, accounting for the experimental results and selectivities observed in our reaction. The following equilibria are proposed for $[H_2Ir(P—P)_2]^+$ (S = solvent):



Scheme 1.

Equilibrium 1 could be operative for seven-membered ring chelates such as diop and prolophos, giving species **b**, which has a vacant site available for coordination of the substrate, unlike the coordinatively saturated dihydride

a. Species b could be responsible for the selective reduction of the C=O bond, by analogy with the species H_3IrP_3 which was proposed to be the active species for such a selectivity in the case of monophosphines [5]. The steric situation in species b will be such that the coordination of the substrate through the olefinic bond would be unfavoured because of steric interactions, whereas an approach through the oxygen atom of the carbonylic group would be much easier.

On the other hand, formation of species c will be preferred in the case of five-membered ring chelates such as chiraphos and prophos. In this case the substrate can coordinate through the C=C bond to the less crowded species c and be selectively reduced to the saturated ketone.

The catalytic results of Table 2 are in agreement with the equilibria proposed in Scheme 1 and can now be interpreted as follows: $[Ir(diop)_2]^+$ and $[Ir(prolophos)_2]^+$ would show a higher selectivity in unsaturated alcohol because of the ring opening with formation, even though in undetectable concentration, of species b, whereas $[Ir(chiraphos)_2]^+$ and $[Ir(prophos)_2]^+$ would only give species c by dissociation of one chelating ligand, hence catalyzing the formation of the saturated ketone. An excess of free diphosphine would shift equilibrium 2 back to the inactive species a, causing the complete inhibition of catalytic activity observed for chiraphos and prophos (see Table 2). Equilibrium 1, on the contrary, would not be directly affected by the presence of free ligand in solution, although the diphosphine in excess could compete for the vacant site available or favor the formation of byproducts, as already suggested for $[Rh(diop)_2]^+$ [13]. Both these possibilities would lead to a decrease in catalytic activity, which is actually observed in the case of $[Ir(diop)_2]^+$ and $[Ir(prolophos)_2]^+$. The formation of byproducts is indeed shown from NMR experiments to occur with $[Ir(diop)_2]^+$.

The following results also support our hypothesis:

(i) in the series $[Ir(Ph_2P(CH_2)_nPPh_2)_2]^+$ (n = 2, 3, 4), selectivity in unsaturated alcohol is found only with $[Ir(dpb)_2]^+$ (n = 4), where a seven-membered metal chelate ring is involved as for diop. $[Ir(dpe)_2]^+$ (n = 2) and $[Ir(dpp)_2]^+$ (n = 3) are both highly selective towards the C=C bond (see Table 3).

(ii) if $[Ir(cod)(P—P)]^+$ is used as catalyst precursor, benzylideneacetone is always reduced to the saturated ketone in high yield with any of the diphosphines used. In the case of $[Ir(cod)(chiraphos)]^+$, for instance, 90% saturated ketone is produced in 5 h. Selectivity changes in the presence of added monophosphine PEt_2Ph: at P(added)/Ir = 2, the unsaturated alcohol is obtained in 71% yield in 24 h. At P(added)/Ir = 1.5, an intermediate situation is observed and both functions are reduced at comparable rates.

These results are consistent with the suggestion that a species with three phosphorus atoms coordinated to the metal is required for the selective reduction of the carbonyl group [5]. The *cis/trans*-dihydride equilibrium could also play a role in the evolution of the catalytic species starting from the cationic complexes. The *cis* isomer in fact should be more reactive than

the *trans* isomer towards the metal chelate ring opening, since in the former two phosphorus atoms have a hydride ligand in the *trans* position. According to this additional hypothesis, the behaviour of $[Ir(chiraphos)_2]^+$ and $[Ir(diop)_2]^+$ with H_2 (see NMR section) would also be consistent with their selectivities in the reduction of benzylideneacetone (see Table 2).

As far as the systems *in situ* are concerned, the presence of the methoxide group in the precursor leads to different species and/or follows a different reaction path from that of the cationic complexes.

We monitored the system formed from $[Ir(cod)(OCH_3)]_2$ and dpe (dpe/Ir = 5) by ^1H NMR. After 1 h in refluxing C_6D_6 under H_2, the solution turns orange-red and a quintet appears in the hydride region (δ — 12.4, J(P—H) = 8.5 Hz). By comparison with literature data [16], we assigned this signal to the species $HIr(dpe)_2$. An analogous experiment carried out using chiraphos as diphosphine also shows the formation of a species which gives a quintet attributable to a similar complex (^1H: δ — 12.8, J(P—H) = 8.5 Hz).

Iridium monohydrides are known to form from $[Ir(cod)(OCH_3)]_2$ and diphosphines in CH_3OH [17]. We think that a similar reaction occurs in our conditions initially, followed by reduction of the diolefin to form $HIr(P—P)_2$ in the presence of excess diphosphine. If so, this species seems to be selective towards the reduction of the carbonyl group independently of the diphosphine used (see Table 1). At low (P—P)/Ir ratios the predominant species in solution should have one coordinated diphosphine, and is very active towards the reduction of the carbon–carbon double bond. At intermediate (P—P)/Ir ratios, the changes in selectivity observed at the beginning of the reaction are probably related to the gradual formation of the bis(diphosphine) species from the precursor.

The differences in catalytic activity and selectivity between the cationic and the *in situ* systems could be attributed to the electronic and steric properties of the five-coordinated iridium(I) monohydride with respect to the six-coordinated iridium(III) dihydride. Complexes of the type $HM(P—P)_2$ (M = Rh, Ir) have been shown to have a nearly tetrahedral or distorted trigonal–bipyramidal arrangement [16a, 18]. The reactivity of this species could be strongly enhanced by its different geometry and charge on the metal as compared to that of the cationic dihydrides. However, the formation of other active species together with the monohydridic one in the system *in situ* cannot be ruled out.

It is noteworthy that a different behaviour is observed if $[Ir(cod)Cl]_2$ is used in place of $[Ir(cod)(OCH_3)]_2$ in the system *in situ* with diop: at (P—P)/Ir = 2 the saturated ketone is obtained in high yield (>90% selectivity), whereas at (P—P)/Ir = 10 the catalytic activity drops to almost zero (compare with runs 8 and 10, Table 1).

The importance of the methoxide group in the precursor is evident from these results, since different active species following different reaction paths are formed and high selectivities in unsaturated alcohol are obtained.

Acknowledgements

This work was supported by the University of Trieste and the Ministry of Education (Rome). One of us (E. C.) acknowledges the Centro CNR di studio sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione (Milan) for financial support.

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