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Preliminary communication

$[Rh(4,7\text{-}Me_2Phen)_2Cl_2]Cl \cdot 2H_2O$: A VERY ACTIVE CATALYST IN HYDROGEN TRANSFER REACTIONS

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Summary

Complexes of the type $[RhChelHx]PF_6$ and $[Rh(Chel)_2Cl_2]Cl$ (Chel = Bipy; Phen; 4,4′-Me_2Bipy; 4,7-Me_2Phen; Hx = 1,5-hexadiene) are very active catalysts in hydrogen transfer from isopropanol to cyclic ketones. The highest rate and stereoselectivity are observed with $[Rh(4,7\text{-}Me_2Phen)_2Cl_2]Cl$.

Some complexes of transition metals assist the transfer of hydrogen from hydrogen donors, mainly primary or secondary alcohols, to organic substrates, such as ketones or α,β-unsaturated ketones. The species with the highest catalytic activity are iridium, ruthenium and rhodium derivatives [1—6].

We have found that rhodium complexes of the type $[Rh(Chel)_2Cl_2]Cl$ (I) and $[Rh(Chel)Hx]PF_6$ (II) (Chel = Bipy; Phen; 4,4′-Me_2Bipy and 4,7-Me_2Phen; Hx = 1,5-hexadiene), which we have shown to be good catalysts for hydrogenation of ketones and olefins [7], also show high catalytic activity in hydrogen transfer from isopropanol to cyclohexanone or substituted cyclohexanones. To obtain catalytic activity it is necessary to operate in the presence of an alkali metal hydroxide, as in the case of analogous complexes containing phosphines [6]. Under the conditions used (Table 1) the reaction due to KOH itself is negligible.

TABLE 1

REDUCTION OF 4-t-BUTYLCYCLOHEXANONE

Reactions were carried out under nitrogen with 2×10^{-3}—5×10^{-4} *M* catalyst concentrations in i-PrOH (0.2% H_2O) (50 ml) containing 0.035 *M* KOH. Reaction time 90 min.

Catalyst	[S]/[cat]	Conversion (%)	*cis*/*trans*
$[Rh(Bipy)_2Cl_2]^+$	675	66.1	1.2
$[Rh(4,4'\text{-}Me_2Bipy)_2Cl_2]^+$	1350	80	1.8
$[Rh(4,4'\text{-}Me_2Bipy)Hx]^+$	1350	46.8	1.1
$[Rh(Phen)_2Cl_2]^+$	675	66.3	2.1
$[Rh(4,7\text{-}Me_2Phen)_2Cl_2]^+$	1350	98.3	4.1
$[Rh(4,7\text{-}Me_2Phen)Hx]^+$	1350	91.9	2.4

As can be seen from Table 1, complexes of type II are less active and less stereoselective than those of type I, and the methyl derivatives are more active than the corresponding complexes with unsubstituted chelating ligands. In particular the 4,7-Me_2Phen derivative, synthesized analogously to $[Rh(Bipy)_2Cl_2]Cl \cdot 2H_2O$ [8], is the most active species and also shows the highest stereoselectivity in producing the thermodynamically less stable alcohol. This complex is about 1000 times more active than $IrCl_3(DMSO)_3$ [2] and at least 10 times as active as rhodium complexes with phosphine or aminophosphine ligands [6] (Table 2).

A high stereoselectivity has also been observed with 3-methylcyclohexanone (*trans/cis* 4.48 with [S]/[cat] 1635; conversion 93.4% in 90 min). In contrast the complex $RhTerpyCl_3$ (Terpy = terpyridyl), which we recently synthesized, is inactive under the conditions described above.

TABLE 2

REDUCTION OF CYCLOHEXANONE

Catalyst	[S]/[cat]	Conversion (%)	Time (h)
$IrCl_3(DMSO)_3$	300	97	72
$RhCl(PPh_3)_3$	400	85	1
$[Rh(4,7\text{-}Me_2Phen)_2Cl_2]Cl$	5000	85	1

References

1 J. Trocha-Grimshaw and H.B. Henbest, Chem. Commun., (1967) 544.
2 M. Gullotti, R. Ugo and S. Colonna, J. Chem. Soc. C, (1971) 2652.
3 S.L. Regen and G.M. Whitesides, J. Org. Chem., 37 (1972) 1832.
4 Y.M. Haddad, H.B. Henbest, J. Husbands, T.R.B. Mitchell and J. Trocha-Grimshaw, J. Chem. Soc. Perkin I, (1974) 596.
5 Y. Sasson and J. Blum, J. Org. Chem., 40 (1975) 1887.
6 P. Svoboda and J. Hetflejš, Coll. Czech. Chem. Commun., 42 (1977) 2177 and ref. therein.
7 G. Mestroni, R. Spogliarich, A. Camus, F. Martinelli and G. Zassinovich, J. Organometal. Chem., 157 (1978) 345.
8 R.D. Gillard, J.A. Osborn and J. Wilkinson, J. Chem. Soc., (1965) 1951.