Journal of Organometallic Chemistry, 184 (1980) C10—C12

Preliminary communication

HYDROGEN TRANSFER REACTIONS FROM ALCOHOLS TO α,β-UNSATURATED KETONES: $[Ir(3,4,7,8\text{-}Me_4\text{-phen})COD]Cl$, A VERY ACTIVE CATALYST PRECURSOR

A. CAMUS, G. MESTRONI and G. ZASSINOVICH
Istituto di Chimica dell'Università di Trieste, 34127 Trieste (Italy)

(Received October 2nd, 1979)

Summary

A high catalytic activity, with turnover up to 900 cycles/min, is displayed by $[Ir(3,4,7,8\text{-}Me_4\text{-phen})COD]Cl$ in hydrogen transfer reactions from propan-2-ol to α,β-unsaturated ketones in a weakly alkaline medium.

As already reported [1,2] complexes of the type [Mchel(L—L)]X (M = Rh, Ir; chel = bipy, phen and methyl-substituted derivatives; X = Cl^-, PF_6^-) show a high catalytic activity in hydrogen transfers from alcohols to ketones in an alkaline medium. This communication presents some preliminary results for such reactions, in which the transfer is from propan-2-ol to α,β-unsaturated ketones.

From the data listed in Tables 1, 2, 3, it can be seen that the double C=C bond undergoes reduction before the carbonyl group. The reaction does not stop when the saturated ketone is formed, and the latter is in turn reduced with

TABLE 1

REDUCTION OF BENZYLIDENACETONE (BA) AND OF BENZYLIDENACETOPHENONE (BAP) WITH VARIOUS CATALYSTS

Catalyst	Substrate	[S]/[cat]	Conversion (%)	Time	Temperature (°C)	Ref.
$IrHCl_2(DMSO)_3$	BAP	20	95	12 h	83°C	3
$RuCl_2(PPh_3)_3$	BA	400	95	1 h	180°C	4
	BAP	400	92	1 h	180°C	
$[Ir(3,4,7,8\text{-}Me_4\text{-phen})COD]Cl$	BA	6800	93	15 min	83°C	
	BAP	4800	94	5 min	83°C	

TABLE 2

REDUCTION OF BENZYLIDENACETONE WITH [Ir(chel)COD]X[a]

Catalyst	[S]/[cat]	[KOH]/[cat]	Rate cycles/min	Conversion (%)	Selectivity (%)
[Ir(4,4'-Me$_2$-bipy)COD]Cl	1700	1.5	17	—	—
[Ir(4,4'-Me$_2$-bipy)COD]PF$_6$	1700	1.5	90	93	98
	3400	3	128	96.5	95
[Ir(4,7-Me$_2$-phen)COD]Cl	1700	1.5	51	84	97
[Ir(4,7-Me$_2$-phen)COD]PF$_6$	3400	3	62	74.5	98.6
[Ir(3,4,7,8-Me$_4$-phen)COD]Cl	1700	1.5	113	88.5	95.8
	3400	3	316	93	90
	6800	6	425	93	89

[a] 34.2 mmol of substrate in 50 ml propan-2-ol (2% water), refluxed under argon. The precursor is activated as reported in ref. 2.

TABLE 3

REDUCTION OF CHALCONE WITH [Ir(chel)COD]X[a]

Catalyst	[S]/[cat]	[KOH]/[cat]	Rate cycles/min	Conversion (%)	Selectivity (%)
[Ir(bipy)COD]PF$_6$	2400	3	43	72	99
[Ir(4,4'-Me$_2$-bipy)COD]PF$_6$	2400	3	110	96	97.5
[Ir(4,7-Me$_2$-phen)COD]PF$_6$	2400	3	125	95.6	99
	4800	3	180	92	99.5
[Ir(3,4,7,8-Me$_4$-phen)COD]Cl	2400	3	480	100	99
	4800	3	904	94	98
	9600	6	463	96	97.5

[a] 24 mmol of substrate in 50 ml propan-2-ol (2% water) refluxed under argon.

a rate comparable to that of the olefinic bond. Under suitable conditions the 3,4,7,8-Me$_4$-phen derivative is extremely efficient as a catalyst. In fact it is 10 000 times more active than the Henbest [3] system and about 100 times more active than the RuCl(PPh$_3$)$_3$, though the latter operates at a higher temperature (Table 1). With a rate of 900 cycles/min the activity of our complex begins to approach that of enzymes, which show an average maximum turnover of 10 000 cycles/min.

The complexes with the other chelates are generally less efficient (Table 2).

Surprisingly the activity of the catalyst is increased by decreasing its concentration (Table 3). Though this is due, at least in part, to the decreasing competitive inhibition exerted by the Cl$^-$ ion (it can be seen from the same table that the rate is increased upon replacing Cl$^-$ by PF$_6^-$), association phenomena at high concentrations of catalyst cannot be excluded.

As mentioned previously for the reduction of ketones, the [Mchel(L—L)]$^+$ species show catalytic activity only in the presence of alkaline hydroxides; however, the results show that the required KOH amount is very small.

The remarkable regioselectivity found with this series of catalysts must be mainly due to the higher affinity towards the active sites of α,β-unsaturated than of saturated ketones (probably by π-coordination of the double C=C bond). In fact, the reaction is of zero-order with respect to the initial substrate, and the reduction of the carbonyl group becomes important only when at least 90% of the starting product has been consumed.

Acknowledgement

Financial support by CNR (Rome) is gratefully acknowledged.

References

1 G. Zassinovich, G. Mestroni and A. Camus, J. Organometal. Chem., 168 (1979) C37.
2 A. Camus, G. Mestroni and G. Zassinovich, J. Mol. Catal., 6 (1979) 231.
3 J. Trocha-Grimshaw and H.B. Henbest, Chem. Commun., (1967) 544.
4 Y. Sasson and J. Blum, J. Org. Chem., 40 (1975) 1887 and ref. therein.