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SELECTIVE HYDROGEN TRANSFER FROM FORMIC ACID TO α,β-UNSATURATED KETONES BY POLYSTYRENE-BOUND $IrCl(CO)(PPh_3)_2$

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Polystyrene-anchored chlorocarbonylbis(triphenylphosphine)iridium has been shown to be a highly stable and active catalyst for the selective transfer hydrogenation of α,β-unsaturated ketones by formic acid.

The application of immobilized transition metal compounds as catalyst in organic processes has been the focus of considerable research in recent years.[1] Yet, to the best of our knowledge, none of these catalysts has ever been used for transfer hydrogenation of unsaturated carbon-carbon double bonds.

We now report the selective hydrogen transfer from formic acid to α,β-unsaturated ketones by polystyrene-attached $IrCl(CO)(PPh_3)_2$ (eq 1).

$$RCH{=}CHCOR' + HCOOH \rightarrow RCH_2CH_2COR' + CO_2 \qquad (1)$$

As an example, a mixture of 0.52 g (2.5 mmol) of benzalacetophenone, 1.89 ml (50 mmol) of formic acid, 1.90 ml of toluene and 114 mg (1.78×10^{-2} meq) of supported iridium catalyst [from $IrCl(CO)(PPh_3)_2$ and 2% crosslinked polymer-bound diphenylphosphine on styrene-divinylbenzene copolymer; Ir content - 3.0%; P/Ir = 2.0][2] was heated under argon[3] at 97 °C for 8 h. GLC analysis (on 1% OV 17/Chromosorb G) indicated the formation of 17% of 1,3-diphenylpropan-1-one. During the process the activity of the polymeric catalyst increased. Thus, by reusing the toluene-washed beads in a second and a third run, 45 and 69% of the saturated ketone were obtained, respectively. In all subsequent turnovers[4], the yield remained constant.

The change in activity (as well as in color) during the first few cycles is attributed to some chemical modifications of the catalyst. This is supported by the gradual appearing of new infrared bands at 2000, 1960 and 1685 cm^{-1}.[5]

Up to 3 x 10^{-2} meq of iridium per 2.5 mmol of substrate, the rate was dependent on the amount of the catalyst. Application of 0.18, 0.44, 0.59, 1.34, 1.72 and 2.18 x 10^{-2} meq of supported $IrCl(CO)(PPh_3)_2$ in the above experiment (third run) led to 1.3, 4.7, 11.9, 49.0, 65.2 and 90.5% of 1,3-diphenylpropan-1-one, respectively. Nearly quantitative yield (96% in the first run of 4 h and 99% in subsequent turnovers) was obtained when 3.11 x 10^{-2} meq of the catalyst was employed. This substrate : catalyst ratio of 1:1.24 x 10^{-2} was generally used for large scale reduction of the chalcone.

As shown for some other polymer-attached catalysts,[5] the activity of the supported iridium complex is sensitive to the nature of the solvent. Replacement of the toluene (in advanced cycles[5]) by ethylene glycol, decane or decalin, increased the conversion of the unsaturated ketone from 62 to 89, 98 and 99%, respectively. The effect proved to be reversible and subsequent runs in toluene yielded once again 62% of the saturated ketone.

Substitution of one phenyl moiety in benzalacetophenone by an alkyl group (of superior electron donating properties) decreased the rate of reaction. Thus, while $C_6H_5COCH{=}CHC_6H_5$ underwent transfer hydrogenation in 17, 45, 69 and 69% in the first four cycles, the corresponding conversions of $C_6H_5COCH{=}CHCH_3$ were only 6, 15, 17 and 30% (the latter figure applied also to subsequent runs).

This observation suggests the coordination of the substrate to the catalyst in the rate determining step. Further support in this assumption was provided by the transfer hydrogenation of $4\text{-}ClC_6H_4COCH{=}CHC_6H_5$, $C_6H_5COCH{=}CHC_6H_5$ and $4\text{-}CH_3COCH{=}CHC_6H_5$ under comparable conditions.[6] The corresponding initial reaction rates were 0.93, 0.82 and 0.22 mmol. $l^{-1}.min^{-1}$.

Comparison of the catalytic power of the supported and free $IrCl(CO)(PPh_3)_2$[7] in reaction 1 revealed that the heterogenized catalyst is the more efficient one.[8] (See Table I). Furthermore, while the recycling of the soluble complex was not possible, the immobilized complex could be reused over and over again. With the aid of atomic emission spectroscopy[9] it was shown that less than 50 ppm of the iridium leached into the solution in the first three runs and practically none at all in subsequent turnovers. The analogous supported $RhCl(CO)(PPh_3)_2$[10], $RhCl(PPh_3)_3$[10] and $RuCl_2(PPh_3)_3$[5] proved, however, to deteriorate in hot formic acid and their performances in reaction 1 were

Table I. Transfer Hydrogenation of Benzalacetophenone by Formic Acid in the Presence of Homogeneous and Polystyrene-Anchored Catalysts under Comparable Conditions[a]

Catalyst	Conversion %		
	1st run	2nd run	3rd run
$IrCl(CO)(PPh_3)_2$	52		
Ⓟ$-PPh_2)_xIrCl(CO)(PPh_3)_{2-x}$[b]	17	45	69
$RhCl(CO)(PPh_3)_2$	5		
Ⓟ$-PPh_2)_xRhCl(CO)(PPh_3)_{2-x}$[c]	14	10	4
$RhCl(PPh_3)_3$	5		
Ⓟ$-PPh_2)_xRhCl(PPh_3)_{3-x}$[d]	4	2	0
$RuCl_2(PPh_3)_3$	44		
Ⓟ$-PPh_2)_xRuCl_2(PPh_3)_{3-x}$[e]	3	2	1

[a] All reactions were carried out under argon at 97 °C for 8 h, and employed 2.5 mmol of the substrate, 50 mmol of formic acid, 1.9 ml of toluene and catalyst that contained 1.8×10^{-2} meq of the metal. [b] Ir = 3.00%. [c] R = 2.14%. [d] R = 0.85%. [e] Ru = 1.40%.

usually worse than those of their homogeneous counterparts (See Table I).

Finally, it should be noted that although formic acid decomposes into H_2 and CO_2 in the presence of homogeneous and resin-anchored $IrCl(CO)(PPh_3)_2$, we have proven that the reduction of benzalacetophenone proceeded by direct hydrogen transfer from the acid rather than via molecular H_2.

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