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$IrCl_2H(P^iPr_3)_2$ as catalyst precursor for the reduction of unsaturated substrates

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Abstract

The complex $IrCl_2H(P^iPr_3)_2$ in the presence of $NaBH_4$ catalyzes hydrogen transfer from 2-propanol to cyclohexanone, 3-methylcyclohexanone, benzylideneacetone, styrene, and cyclohexadienes. Under the reaction conditions, the compound $IrH_5(P^iPr_3)_2$, is formed and is the actual catalyst precursor. The complex $IrCl_2H(P^iPr_3)_2$ reacts with hydrogen to give the dihydrido complex $IrClH_2(P^iPr_3)_2$. In the presence of unsaturated substrates such as benzylideneacetone, phenylacetylene, styrene, and 1,4-cyclohexadiene, this reaction is inhibited, and reduction of these substrates takes place. The compound $IrClH_2(P^iPr_3)_2$ is itself also an active catalyst for the hydrogenation of the above-mentioned substrates.

1. Introduction

We have previously reported the synthesis [1], reactivity [1–5], and catalytic properties [6–11] of the complex $OsClH(CO)(P^iPr_3)_2$, which in the presence of KOH or $NaBH_4$ is an efficient catalyst in the hydrogen transfer from 2-propanol to cyclohexanone [6], acetophenone [6], benzylideneacetone [7], and phenylacetylene [8]. Under an atmosphere of hydrogen, it also catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene, diphenyl- and phenylacetylene [9,10]. In continuation of our work in this field, we describe here the results of a study of the catalytic behaviour of the complex $IrCl_2H(P^iPr_3)_2$ (**1**) [12], which is formally isoelectronic and isostructural [13] with the above-mentioned osmium complex.

2. Results and discussion

2.1 Hydrogen transfer reactions

The catalytic activity of $IrCl_2H(P^iPr_3)_2$ (**1**) in the reduction of unsaturated substrates by hydrogen transfer from 2-propanol is very low in the absence of a co-catalyst (see Table 1). Thus no more than 2% of 3-methylcyclohexanone is converted into the corresponding alcohol in 22 h. Similar behaviour is observed with styrene and benzylideneacetone as substrates. This, particularly in the latter case, is in contrast with the behaviour of the complex $OsClH(CO)(P^iPr_3)_2$, which catalyzes the reduction of benzylideneacetone and benzylideneacetophenone quite efficiently [7]. A reasonable explanation of this significant difference in catalytic activity is given by the fact, that, in contrast to **1** $OsClH(CO)(P^iPr_3)_2$ forms stable adducts with hydrogen, oxygen, olefins and alkynes, a difference that can be attributed to the stronger *trans* influence of the hydride ligand in **1**. This pronounced hydridic character is also reflected in the strong high field shift of the hydride resonance in **1** to −49 ppm [12], compared with −32 ppm for that in $OsClH(CO)(P^iPr_3)_2$ [1].

Addition of $NaBH_4$, however, gives rise to a significant increase in the catalytic activity of **1**. Similar behaviour is also observed for the complex $OsClH(CO)(P^iPr_3)_2$ [6], which reacts with $NaBH_4$ to give initially the tetrahydroborate compound $OsH(BH_4)(CO)(P^iPr_3)_2$ [3]. This complex decomposes, however, under the catalytic conditions to give the tetrahydride

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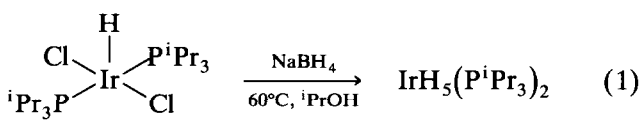
TABLE 1. Hydrogen transfer from 2-propanol to ketones catalyzed by **1** [a]

Co-catalyst	Substrate	Time (h)	Products (%)
$NaBH_4$	Cyclohexanone	24	Cyclohexanol (85)
	3-Methylcyclohexanone	22	3-Methylcyclohexanol (2)
$NaBH_4$	3-Methylcyclohexanone	24	*cis*-3-Methylcyclohexanol (37)
			trans-3-Methylcyclohexanol (57)
	Benzylideneacetone	16	4-Phenyl-2-butanone (2)
$NaBH_4$	Benzylideneacetone	5	4-Phenyl-2-butanone (86)
			4-Phenyl-2-butanol (6)

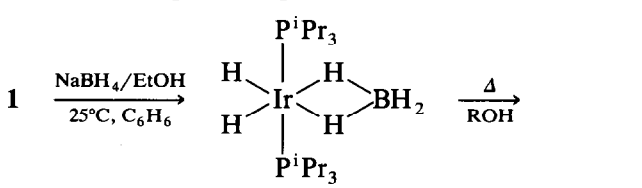
[a] Reaction conditions: $[M] = 2.5 \times 10^{-3}$ M, [Sub]/[M] = 100, $[NaBH_4]/[M] = 5$; solvent, 2-propanol; $T = 83°C$.

$OsH_4(CO)(P^iPr_3)_2$ [6], which catalyzes the hydrogen transfer via an $OsH_2(CO)(P^iPr_3)_2$ intermediate. Correspondingly, **1** reacts with excess $NaBH_4$ under the catalytic conditions to give the pentahydride complex $IrH_5(P^iPr_3)_2$ (**2**) (eqn. (1)).



(1) (2) (1)

If the reaction of **1** with $NaBH_4$ is carried out in apolar solvents, such as benzene, in the presence of only small amounts of ethanol, the tetrahydroborate compound $IrH_2(BH_4)(P^iPr_3)_2$ (**3**) is formed as the main product. Compound **3** is stable in aprotic solvents but decomposes readily on heating in alcohols to give the pentahydrido complex **2** (eqn. (2)).



(3) (2) (2)

The preparation of related complexes to **3** with other phosphine ligands has been previously reported by Shaw and co-workers [14].

As the trihydride $IrH_3(P^iPr_3)_2$ (**4**), which is electronically equivalent to $OsH_2(CO)(P^iPr_3)_2$, can be generated from **2** by loss of one molecule of hydrogen, we assume that it is transiently formed during the reactions given in Table 1. The intermediacy of the trihydride **4** in catalytic reactions with the pentahydrido compound **2** has recently been demonstrated by Halpern *et al.* [15].

Complex **4** generated under the above mentioned conditions catalyzes the hydrogen transfer from 2-propanol to cyclohexanones, benzylideneacetone, styrene, and cyclohexadienes (see Tables 1 and 2). Although in the case of α,β-unsaturated ketones, either the C=C or the C=O bond may be reduced, the results given in Table 1 reveal that hydrogenation of the carbon–carbon double bond is clearly preferred. No unsaturated alcohol could be detected. This selectivity is most probably due to the preferential coordination of the C=C bond to the metal, since the coordinating ability of the carbonyl group in α,β-unsaturated ketones relative to that of saturated ketones is decreased by conjugational effects [16].

The pentahydrido complex $IrH_5(P^iPr_3)_2$ is known to be an extremely efficient catalyst or catalyst precursor for the hydrogen transfer from 2-propanol to t-butylethylene [15]. However, its catalytic activity in the reduction of styrene is far lower. At 83°C with initial concentrations of 0.25 M styrene and 2.5×10^{-3} M catalyst in 2-propanol, a conversion of 24% is observed after 7 h. In general, arylalkenes are less effective substrates since they can undergo unusual rearrangements to give aryl metal complexes that are inactive in hydrogen transfer reactions [17,18].

With 1,4-cyclohexadiene as a substrate, different catalytic reactions take place. Initially, the rapid isomerization of the 1,4-isomer to the thermodynamically more stable 1,3-isomer occurs. Subsequently, **2** catalyzes the disproportionation of the so formed 1,3-cyclohexadiene to cyclohexene and benzene. This is clearly confirmed by the observation that even after

TABLE 2. Hydrogen transfer from 2-propanol to 1,4-cyclohexadiene catalyzed by **1** [a]

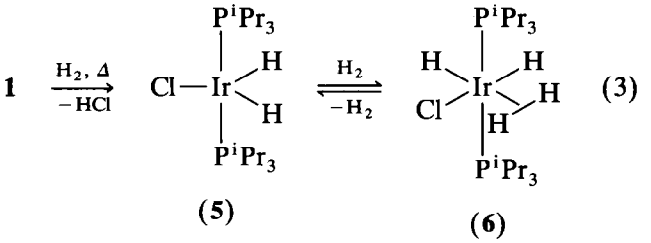
Time (min)					
30	0	7	27	58	8
60	0	14	21	46	19
90	0	16	20	44	20
180	0	26	16	35	23

[a] Reaction conditions: $[M] = 2.5 \times 10^{-3}$ M, $[1,4\text{-}C_6H_8]_{initial} = 0.25$ M; solvent, 2-propanol; $T = 83°C$.

180 min no acetone could be detected by GLC, indicating that the solvent had not been dehydrogenated at that point. However, after longer reaction times, some dehydrogenation of the solvent was observed. After 24 h, GLC analysis of the resulting mixture revealed a composition of 3% 1,4-cyclohexadiene, 6% 1,3-cyclohexadiene, 37% benzene, 52% cyclohexene, and 2% of cyclohexane. There are precedents for similar catalytic reactions involving the cleavage of C–H bonds in the presence of the pentahydrido complex **2** [19]. With olefins containing more than three carbon atoms, equimolar amounts of dienes and saturated hydrocarbons are formed. The dienes are linear, conjugated, and predominantly in the *trans,trans*-configuration [20].

2.2. Hydrogenation reactions

Under an atmosphere of hydrogen, **1** is transformed quantitatively to the dihydrido complex $IrClH_2(P^iPr_3)_2$ (**5**). In the presence of an excess of hydrogen, **5** is in equilibrium with the η^2-dihydrogen compound **6**, which in the meantime has been described independently by Jensen and co-workers [21] (eqn. (3)).



(3)

(5) (6)

According to a recent report by Vol'pin *et al.* [22], the reaction of **1** with H_2 proceeds by initial formation of $IrCl_2H(H_2)(P^iPr_3)_2$, which is unstable under normal conditions but can be observed by low temperature NMR spectroscopy under an atmosphere of hydrogen. After oxidative addition of the coordinated hydrogen molecule, reductive elimination of HCl takes place and the dihydride **5** is formed.

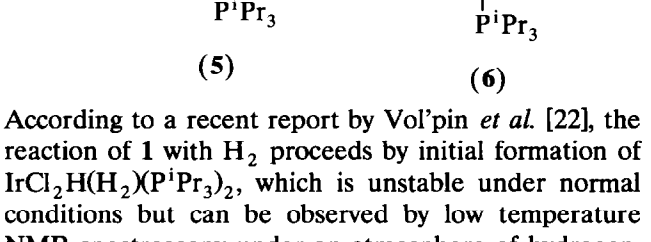
In the presence of olefins such as styrene, cyclohexadiene, and benzylideneacetone, or of phenylacetylene, the conversion of **1** into **5** is inhibited, and instead catalytic hydrogenation of the unsatured substrates occurs at considerable rates (see Table 3). Benzylideneacetone and phenylacetylene are reduced selectively to the saturated ketone and styrene, respectively. However, the selectivity towards hydrogenation of 1,4-cyclohexadiene is poor, although no disproportionation to cyclohexene and benzene is observed in this case.

Since the reduction of styrene takes place faster than that of phenylacetylene (see Table 3), the origin of the observed selectivity cannot be kinetic in nature. A similar effect has been observed for the osmium complex $OsClH(CO)(P^iPr_3)_2$, which catalyzes the hydrogenation of phenylacetylene via the vinyl intermediate $OsCl(E\text{-}CH{=}CHPh)(CO)(P^iPr_3)_2$. Kinetic studies reveal that the formation of such vinyl compounds is the step that determines the selectivity [10]. Although the reaction of **1** with phenylacetylene gives only mixtures of products from which no vinyl complex could be isolated, the use of the more active alkyne HC_2CO_2Me gave $IrCl_2(E\text{-}CH{=}CHCO_2Me)(P^iPr_3)_2$ (**7**) in good yields. Compound **7** reacts with H_2 spontaneously by elimination of the vinyl ligand and re-formation of **1** (eqn. (4)).

TABLE 3. Hydrogenation of unsatured organic substrates [a]

Catalyst	Substrate	Time (h)	Products (%)
1	Benzylideneacetone	24	4-Phenyl-2-butanone (31)
5	Benzylideneacetone	2	4-Phenyl-2-butanone (37)
1	1,4-Cyclohexadiene	5	Cyclohexane (14) Cyclohexene (59)
5	1,4-Cyclohexadiene	2	Cyclohexane (8) Cyclohexene (50.5)
1	Styrene	3	Ethylbenzene (97)
5	Styrene	0.5	Ethylbenzene (97)
1	Phenylacetylene	20	Ethylbenzene (2) Styrene (33)
5	Phenylacetylene	10 min	Ethylbenzene (44) Styrene (55)

[a] Reaction conditions: $[M] = 2.5 \times 10^{-3}$ M, [Sub] = 0.25 M, $p(H_2)$ = 1 atm; solvent, 2-propanol; $T = 60°C$.



(4)

(7)

The results shown in eqn. (4) confirm the assumption that vinyl compounds such as **7** participate in the catalytic cycle, and as in the case of osmium are probably the origin of the observed selectivity.

The dihydrido complex $IrClH_2(P^iPr_3)_2$ (**5**) itself is a catalyst that is even more active than **1** under molecular hydrogen, although less selective in the hydrogenation of phenylacetylene (see Table 3). This decrease in selectivity can be attributed to the fact that **5** reacts with an excess of phenylacetylene to give the trisalkynyl compound $Ir(C_2Ph)_3(P^iPr_3)_2$ [23], which causes the reaction to follow a different route leading to simultaneous reduction of C≡C and C=C bonds. Kinetic studies of the hydrogenation of benzylideneacetone in the presence of **5** have been described elsewhere [24].

3. Concluding remarks

The investigations described above have revealed that the complex $IrCl_2H(P^iPr_3)_2$ is a useful catalyst or

catalyst precursor for the reduction of unsatured organic substrates by hydrogen transfer from 2-propanol or direct hydrogenation in an atmosphere of H_2. Since $IrCl_2H(P^iPr_3)_2$ is formally isoelectronic and isostructural to the osmium compound $OsClH(CO)(P^iPr_3)_2$, there is substantial similarity in the catalytic behaviour of these two complexes. Finally, it should be noted that reduction of organic substrates by molecular hydrogen is in many cases more effective, but sometimes the application of hydrogen transfer catalysis leads to interesting changes in selectivity.

4. Experimental details

All manipulations were conducted with vigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. Styrene and 1,4-cyclohexadiene were purified by passage through a column of active neutral alumina before use. Cyclohexanone, 3-methylcyclohexanone, and phenylacetylene were purified by distillation. Benzylideneacetone (Merck 98%) was used without further purification. The compounds $IrCl_2H(P^iPr_3)_2$ [12], $IrClH_2(P^iPr_3)_2$ [12], and $IrH_5(P^iPr_3)_2$ [20,23] were prepared by published methods.

Analysis of the catalytic reactions was carried out on a Perkin–Elmer 8500 gas chromatograph with a flame ionization detector. A β,β-oxydipropionitril (15%) on Chromosorb 6HP 80/100 mesh column (4 m × 3 mm) was used at 60°C for 1,4-cyclohexadiene analysis. The other substrates were analyzed using a FFAP on Chromosorb 6HP 80/100 mesh column (3.6 m × 3 mm) at 120°C (cyclohexanone, 3-methylcyclohexanone), 175°C (styrene and phenylacetylene), or 200°C (benzylideneacetone). The stoichiometric reactions were carried out by use of Schlenk techniques. NMR spectra were recorded on a 90 MHz Jeol FX-90Q instrument, IR spectra on a Perkin–Elmer 1420 spectrometer.

4.1. Hydrogen transfer reactions

These reactions were carried out under nitrogen in refluxing 2-propanol with magnetic stirring. The equipment consisted of a 50-ml round-bottomed flask fitted with a reflux condenser and provided with a serum cap.

In a typical procedure, a solution of $IrCl_2H(P^iPr_3)_2$ (0.02 mmol) in 4 ml 2-propanol was refluxed for 1 h and 2 mmol of substrate in 4 ml of 2-propanol were then injected. In the presence of $NaBH_4$, the procedure was as follows. To a solution of $IrCl_2H(P^iPr_3)_2$ (0.02 mmol) in 2 ml of 2-propanol was added $NaBH_4$ (3.78 mg, 0.1 mmol) in 2 ml of 2-propanol. The resulting solution was then refluxed for 1 h and 2 mmol of substrate in 4 ml of 2-propanol were then injected.

4.2. Hydrogenation reactions

A degassed solution of the catalyst (0.02 mmol) in 2-propanol (4 ml) was syringed through a silicon septum into a 25-ml flask attached to a gas burette, which was in turn connected to a Schlenk manifold. The system was evacuated and refilled with hydrogen three times and the flask then immersed in a constant temperature bath (60°C). The substrate (2 mmol), dissolved in 4 ml degassed 2-propanol, was then injected through the septum and the mixture vigorously shaken during the run.

4.3. Reaction of 1 with $NaBH_4$: preparation of $IrH_2(BH_4)(P^iPr_3)_2$ (3)

To a solution of 71 mg $IrCl_2H(P^iPr_3)_2$ (0.12 mmol) in 10 ml of benzene were added 91 mg $NaBH_4$ (2.4 mmol) and 2 ml of ethanol were added dropwise at room temperature with vigorous stirring. Within 10 min, the colour of the reaction mixture had changed from red to colourless. After 30 min, the solvents were removed *in vacuo*, the pale yellow residue extracted with 5 ml of benzene, and the solution concentrated *in vacuo* to *ca.* 1 ml, then chromatographed on neutral Al_2O_3 (act. grade V). The colourless crystalline product was always contaminated with 5–10% of $IrH_5(P^iPr_3)_2$ (as shown by ^{31}P NMR spectroscopy), which could not be removed by recrystallization from hexane. IR (C_6H_6): ν 2415 ($B-H_{as}$), 2340 ($B-H_s$), 2165 cm^{-1} (Ir–H). ^1H NMR (C_6D_6): δ −19.30 (dt, $J(PH) = 15.1$, $J(HH) = 7.3$ Hz; IrH_2); −7.1 (br, IrH_2BH_2); 1.15 (dvt, N 13.2, $J(HH) = 6.8$ Hz; $PCHCH_3$); 2.13 (m, $PCHCH_3$). ^{31}P NMR (C_6D_6): δ 43.8 (s, t in off-resonance).

4.4. Reaction of 1 with H_2: formation of $IrClH_2(P^iPr_3)_2$ (5)

A solution of 56 mg $IrCl_2H(P^iPr_3)_2$ (0.10 mmol) in 5 ml of 2-propanol was frozen in liquid air, and the Schlenk tube evacuated and refilled with hydrogen. The mixture was then heated at 60°C for 2 h and afterwards the solvent was removed *in vacuo*. The yellow-orange residue was dissolved in *ca.* 1 ml of benzene and the solution chromatographed on neutral Al_2O_3 (act. grade V) to give 49 mg $IrClH_2(P^iPr_3)_2$ (93%). The product was identified by comparison of the spectroscopic data with those of an authentic sample [12].

4.5. Reaction of 1 with HC_2CO_2Me: preparation of $IrCl_2(E\text{-}CH{=}CHCO_2Me)(P^iPr_3)_2$ (7)

A solution of 65 mg $IrCl_2H(P^iPr_3)_2$ (0.11 mmol) in 6 ml of benzene was treated with 30 μl HC_2CO_2Me (28 mg, 0.33 mmol) and the mixture was heated at 60°C for 5 h. After removal of the solvent *in vacuo*, the red oily

residue was dissolved in *ca.* 1 ml of benzene and the solution chromatographed on neutral Al_2O_3 (act. grade V) to give 47 mg $IrCl_2(E\text{-}CH{=}CHCO_2Me)(P^iPr_3)_2$ (63%); m.p. 148°C (dec.). Anal. Found: C, 39.42; H, 7.39. $C_{22}H_{47}Cl_2IrO_2P_2$ calc.: C, 39.52; H, 7.09%. IR (KBr): ν 1702 (C=O), 1553 (C=C) cm^{-1}. ^1H NMR (C_6D_6): δ 1.26 (dvt, *N* 13.6, *J*(HH) = 7.1 Hz; PCHCH_3); 3.06 (m, PC*H*CH$_3$); 3.50 (s, OCH_3); 6.39 (dt, *J*(PH) = 1.9, *J*(HH) = 13.6 Hz, IrCH=C*H*); 10.83 (dt, *J*(PH) = 1.5, *J*(HH) = 13.6 Hz, IrC*H*=CH). ^{31}P NMR (C_6D_6): δ 10.14 (s).

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