Notes

Hydrogenation of Benzylideneacetone Catalyzed by IrClH2(PiPr3)2: Kinetic Evidence for the Participation of an Ir(η2-H2) Complex in the Activation of Molecular Hydrogen

Miguel A. Esteruelas,[†] Juana Herrero,[†,‡] Ana M. López,[†]
Luis A. Oro,*,[†] Michael Schulz,[§] and Helmut Werner*,[§]

Departamento de Química Inorgánica, Instituto de Ciencia
de Materiales de Aragón, Universidad de Zaragoza-CSIC,
E-50009 Zaragoza, Spain, and Institut für Anorganische
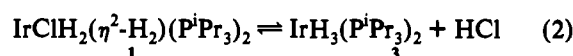Chemie der Universität Würzburg, Am Hubland,
D-8700 Würzburg, Germany

Since the first report by Kubas et al. on the coordination of molecular hydrogen to a transition metal,[1] such compounds have been intensively studied.[2] A quite common property of these complexes seems to be that the coordinated dihydrogen ligand is readily deprotonated.[3] The hydridic character of this ligand has prompted speculation that η2-H2 compounds may be key intermediates of the heterolytic hydrogen activation in catalytic hydrogenation processes. According to this, Crabtree[4] has proposed that the ruthenium complex RuCl2(PPh3)3, a highly effective olefin hydrogenation catalyst,[5] could activate H2 heterolytically via the dihydrogen complex RuCl2(η2-H2)(PPh3)3; but, unfortunately, there is no yet direct experimental evidence to substantiate this proposal.
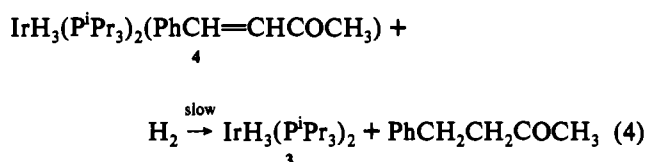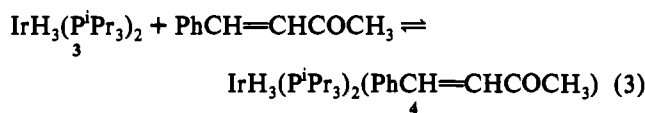
Jensen et al. have recently reported the isolation and characterization of the neutral dihydrogen iridium compound IrClH2(η2-H2)(PiPr3)2 (1).[6] In solution, 1 establishes an equilibrium with IrClH2(PiPr3)2 (2) through the reversible loss of H2. We have now found experimental evidence for the participation of 1 in the activation of H2, as an intermediate in the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by 2.

The hydrogenation reactions were carried out in propan-2-ol at 60 °C.[7] No reduction of the organic substrate was observed under argon, showing that hydrogen transfer from the solvent does not represent an important mechanistic pathway in the

catalysis. In order to determine the mechanism of this catalytic reaction, the kinetics of the process were studied. Initial hydrogenation rates were obtained from gas uptake experiments (Figure 1). To determine the rate dependence on the various reaction components, hydrogenation runs were performed at different concentrations of 2 and benzylideneacetone and at different hydrogen pressures (Table I). The reaction rate is first order with respect to the concentrations of 2 and of substrate and second order with respect to hydrogen pressure.[8] The second-order dependence of the rate on the hydrogen pressure strongly suggests that 2 is the catalyst precursor and, under catalytic conditions, it is in equilibrium with the dihydrogen complex IrClH2(η2-H2)(PiPr3)2 (1),[9] which subsequently loses HCl to generate the active species IrH3(PiPr3)2 (3), as shown in eqs 1 and 2.

$$IrClH_2(P^iPr_3)_2 + H_2 \rightleftharpoons IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2 \quad (1)$$
$$\underset{2}{} \qquad\qquad\qquad\qquad \underset{1}{}$$

$$IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2 \rightleftharpoons IrH_3(P^iPr_3)_2 + HCl \quad (2)$$
$$\underset{1}{} \qquad\qquad\qquad \underset{3}{}$$

In accordance with this, the hydrogenation of benzylideneacetone was found to be inhibited by the addition of HCl in propan-2-ol. The initial rate was inversely proportional to the concentration of added HCl (Figure 2).[10] The formation of 3 is also supported by the reaction of 2 with molecular hydrogen in the presence of Et3N; this leads to IrH5(PiPr3)2,[12] which is known to be an efficient catalyst precursor via the intermediate 3.[13] In light of these results, the following reaction steps are consistent with the catalytic cycle:

$$IrH_3(P^iPr_3)_2 + PhCH{=}CHCOCH_3 \rightleftharpoons$$
$$\underset{3}{}$$

$$IrH_3(P^iPr_3)_2(PhCH{=}CHCOCH_3) \quad (3)$$
$$\underset{4}{}$$

$$IrH_3(P^iPr_3)_2(PhCH{=}CHCOCH_3) +$$
$$\underset{4}{}$$

$$H_2 \xrightarrow{\text{slow}} IrH_3(P^iPr_3)_2 + PhCH_2CH_2COCH_3 \quad (4)$$
$$\qquad\qquad \underset{3}{}$$

With regard to the kinetic data, there is no doubt that the reaction of 4 with H2 is the rate-determining step.

Although numerous reports on η2-H2 complexes have appeared recently,[14] the role of these compounds in homogeneous catalytic hydrogenation reactions have received relatively little attention. Theoretical studies on the oxidative addition of molecular

† Universidad de Zaragoza-CSIC.
‡ On leave from the Universidad de Cantabria.
§ Universität Würzburg.
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(7) Reaction conditions: [2] = 3 × 10⁻³ M; [benzylideneacetone]/[2] = 30; solvent = propan-2-ol; *T* = 60 °C; *P*(H₂) = 1 atm. Conversion of benzylideneacetone was found to be 97% after 11 h (GC yield: 97% 4-phenylbutan-2-one, 3% benzylideneacetone).
(8) Plots of log (–d*V*/d*t*) versus log [2], log (–d*V*/d*t*) versus log [substrate], and log (–d*V*/d*t*) versus log *P*(H₂) yield straight lines of slopes 1.0, 1.1, and 2.2, respectively.
(9) The presence of 1 under catalytic conditions was confirmed by the ³¹P NMR spectrum of the catalytic solution, which shows a broad singlet about 51 ppm that can be assigned to equilibrium shown in eq 1.[6]
(10) It has been previously reported that the IrH₂Cl(HCl)(PiPr₃)₂ adduct can be involved in equilibrium with 2 and HCl.[11] However, the catalytic solution behavior of 2 does not suggest further equilibria involving some HCl adduct. Under catalytic conditions, the presence of IrH₂Cl(HCl)(PiPr₃)₂ should lead to a nonlineal relationship between 1/(–d*V*/d*t*) and [HCl].
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(12) Similarly, 2 reacts smoothly with H₂ (1 atm, 20 °C) in 50% NaOH/benzene two-phase systems in the presence of triethylbenzylammonium chloride as a phase-transfer catalyst to form IrH₅(PiPr₃)₂: Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.
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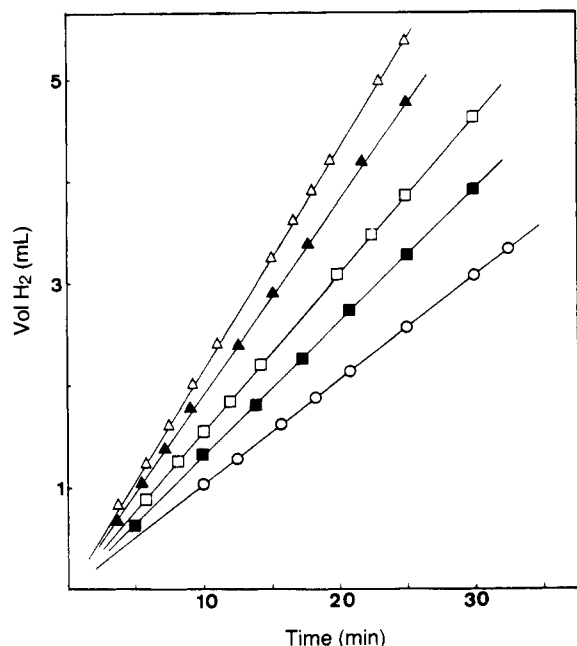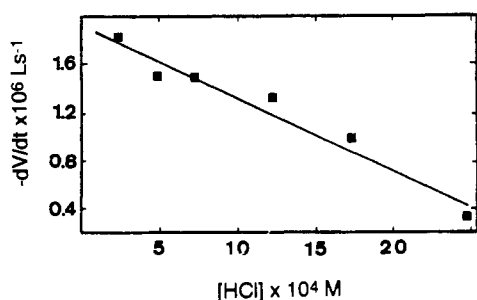
Figure 1. H_2 gas uptake plots for the $IrClH_2(P^iPr_3)_2$-catalyzed hydrogenation of benzylideneacetone to 4-phenylbutan-2-one in propan-2-ol at 60 °C ($P(H_2)$ = 1 atm, $[IrClH_2(P^iPr_3)_2]$ = 1.93 × 10^{-3} M). [Benzylideneacetone] = 0.25 M (O), 0.30 M (■), 0.35 M (□), 0.40 M (▲), 0.49 M (△).

Table I. Kinetic Data for the Hydrogenation of Benzylideneacetone to 4-Phenylbutan-2-one Catalyzed by $IrClH_2(P^iPr_3)_2$[a]

$10^3[Ir]$, M	[benzylideneacetone], M	$P(H_2)$, atm	$10^4[HCl]$, M	$10^6(-dV/dt)$, L s^{-1}
1.34	0.30	1		1.73
1.93	0.30	1		2.16
2.59	0.30	1		3.33
2.97	0.30	1		3.60
1.93	0.25	1		1.73
1.93	0.35	1		2.56
1.93	0.40	1		3.16
1.93	0.49	1		3.58
1.93	0.30	0.53		0.48[b]
1.93	0.30	0.68		1.13[b]
1.93	0.30	0.78		1.15[b]
1.93	0.30	0.88		1.46[b]
1.93	0.30	1	2.47	1.83
1.93	0.30	1	4.95	1.50
1.93	0.30	1	7.42	1.50
1.93	0.30	1	12.37	1.33
1.93	0.30	1	17.32	1.00
1.93	0.30	1	24.75	0.33

[a] In 2-propanol at 60 °C. [b] Corrected to P = 1 atm.

Figure 2. Plot of the rate of hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by $IrClH_2(P^iPr_3)_2$ in propan-2-ol at 60 °C versus [HCl] ($P(H_2)$ = 1 atm, $[IrClH_2(P^iPr_3)_2]$ = 1.93 × 10^{-3} M, [benzylideneacetone] = 0.30 M).

hydrogen to $RhCl(PPh_3)_3$ suggest the existence of a nondetectable $Rh(\eta^2\text{-}H_2)$ intermediate.[15] In agreement with this proposal, spectroscopic observations indicate that the solutions of some

η^2-H_2 compounds contain a dihydride equilibrium fraction.[16] On the other hand, the η^2-H_2 ligand may behave as a good leaving group;[17] this weak Lewis base character permits it to stabilize unsaturated species in solution, without affecting the coordination of the substrate to the metal center. In this respect, several catalytic systems based upon this concept have been reported.[18] In addition, we provide in this note experimental evidence for the participation of a η^2-H_2 complex in the activation of molecular hydrogen in a catalytic process. The conclusion is that the $IrClH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ complex is an intermediate in the activation of hydrogen on going from $IrClH_2(P^iPr_3)_2$ to $IrH_3(P^iPr_3)_2$.

Experimental Section

Complex 2 was prepared as described in the literature.[19]

Kinetic Studies. The catalytic reactions were followed, at constant pressure, by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). The analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb GHP 80/100-mesh (3.6 m × $^1/_8$ in.) column at 220 °C. In a typical procedure, a degassed solution of 2 in propan-2-ol (4 mL) was syringed through a silicone septum into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenk manifold. The system was evacuated and refilled with hydrogen three times, and the flask was then immersed in a 60 °C bath. The substrate, dissolved in deaerated propan-2-ol (4 mL), was subsequently introduced through the septum, and the mixture was vigorously shaken during the run. The reaction products were identified by comparison of their retention times with those observed for pure samples. Plots of kinetic data were fitted by conventional linear regression methods.

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