Hydrogenation of single and multiple N–N or N–O bonds by Ru(II) catalysts in homogeneous phase

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Abstract

The ruthenium(II) complexes $RuH_2(CO)_2(P''Bu_3)_2$, $RuH_2(CO)_2(PPh_3)_2$, and $RuH_2(PPh_3)_4$ are catalytically active in the hydrogenation of organic substrates containing a N=N, N(O)=N or NO_2 group. The reduction of the first two groups leads to hydrazine as intermediate and amine as the final product, while reducing a NO_2 group the corresponding amine is selectively formed. A complete conversion was reached, depending on temperature, catalyst and substrate concentration. The catalysts are also active in the hydrogenolysis of an N–N group giving the corresponding amine with a 97.3% conversion using $RuH_2(PPh_3)_4$ as catalyst. A first-order reaction rate with respect to substrate, catalyst or hydrogen pressure was detected in all cases. Finally, the activation parameters and the kinetic constants of these reactions were calculated. In the hydrogenation of azobenzene, the rate determining step involves an associative or a dissociative step depending on the catalyst employed while in the hydrogenation of all other substrates an associative rate determining step is always involved. A catalytic cycle is suggested for the hydrogenation of azobenzene, taking into account the intermediate complexes identified in the reaction medium.
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1. Introduction

Amines play an important role in the synthesis of organic chemicals since they are intermediates in the production of agrochemicals [1], dyes [2], fibers [3], pharmaceuticals [4] and others [5]. The hydrogenation of a CN, N=N or NO_2 group may be an important route to produce a variety of amines such as aniline, benzylamine, ecc.

The catalytic hydrogenation of nitro- [6] nitrile- [7,8] and azo-compounds [9] under a high pressure of hydrogen has been realised either in the presence of supported catalysts [10] or in homogeneous phase [11]. In contrast to the abundance of processes based on heterogeneous hydrogenation, very few examples are reported for the

process in homogeneous phase. Particular relevance was given to the heterogeneous hydrogenation in the presence of Pd or other transition metals supported on carbon, alumina or silica [12]. The products formed in the heterogeneous or homogeneous process are the same: primary amines were formed from the hydrogenation of nitro- [6] or azo-compounds [9] while a mixture of primary, secondary and tertiary amines were obtained from nitriles [7,8].

Finally, the studies on the activation of multiple nitrogen-nitrogen bonds play a relevant role to understand the mechanism involved in the reduction of nitrogen to produce ammonia [13]. The industrial process requires high temperature and pressure, while the transformation of atmospheric nitrogen into ammonia or its derivatives is obtained by natural processes in very mild conditions [14]. Transition metal are however involved both in the industrial and biological processes.

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In this paper, we report some recent achievement on the catalytic activity of Ru(II) dihydride complexes in the homogeneous hydrogenation of a R–N=N–R, R–N(O)=N–R, or RNO_2 group and in the hydrogenolysis of a R–NH–NH–R compound (R = Ph). The $RuH_2(CO)_2(P^nBu_3)_2$ (**1**), $RuH_2(CO)_2(PPh_3)_2$ (**2**), $RuH_2(PPh_3)_4$ (**3**), and $RuH_2[P(OEt)_3]_4$ (**4**) complexes were chosen in consideration of their well-known catalytic activity in the hydrogenation of unsaturated substrates such as alkenes and carbonylic compounds [15].

Furthermore, the influence of various reaction parameters and ligands coordinated to ruthenium(II) complexes, affecting the electronic or steric properties of catalysts were investigated.

The activation parameters and the kinetic constants of these reactions were also calculated to collect informations on the reaction mechanism.

2. Experimental

2.1. Instruments and materials

Quantitative analyses were performed using a Shimadzu GC14 chromatograph equipped with two FID detectors, using 2 m packed columns filled with FFAP (free fatty acid phase) or CW 20 M + KOH as stationary phase. Quantitative GC analyses were performed using p-xylene as internal standard. The response factors of reagents and products versus p-xylene were detected. The identity of the products was confirmed by GC–MS using a Shimadzu apparatus (GCMS-QP5050A) equipped with a capillary column SP^{TM}-1 (length 30 m, diameter 0.25 mm, film thickness 0.1 μm).

HPLC analyses were performed using a Gilson apparatus: two pumps Gilson 305 and 306 having a 10 μl/min head, autosampling Gilson 231 with dilution Gilson 401, UV detector Gilson 116. A Perkin–Elmer Analytical C_{18} column having dimensions 250×4.6 mm, operating in a reverse phase was employed.

Elemental analyses were performed with a Perkin–Elmer Analyser Model 2400 Series II CHNS/O.

IR spectra were recorded with a Perkin–Elmer Model 1760 FT-IR spectrometer.

^1H, ^{13}C and ^{31}P NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^1H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P NMR, using solutions in deuterated solvents. $SiMe_4$ was used as external standard for ^1H and ^{13}C NMR, H_3PO_4 (85%) for ^{31}P NMR (signals reported as positive downfield to the standard). ^{13}C and ^{31}P NMR spectra were acquired using a broad band decoupler.

All manipulations were routinely carried out under a nitrogen atmosphere using standard Schlenk techniques.

Hydrogenations were carried out in a Parr Model 4759 stainless steel autoclave (150 mL) electrically heated and equipped with a magnetic drive stirrer or in a home made stainless steel high pressure vessel (150 mL) heated and rocked in a thermostated oil bath.

Tetrahydrofuran (THF) was dried and deoxygenated by refluxing and distilling over sodium/potassium amalgam under nitrogen atmosphere.

The following ruthenium complexes were prepared according to the literature: $Ru(CO)_2(CH_3COO)_2(P^nBu_3)_2$ [16], $Ru(CO)_2(CH_3COO)_2(PPh_3)_2$ [17], $RuH_2(CO)_2(P^nBu_3)_2$ (**1**) [18], $RuH_2(CO)_2(PPh_3)_2$ (**2**) [19], $RuH_2(PPh_3)_4$ (**3**) [20], $RuH_2[P(OEt)_3]_4$ (**4**) [21]. The spectroscopic characteristics of these complexes were in agreement with the data reported.

Azobenzene was prepared according to the Nystrom and Brown method [22].

N,N'-Diphenylhydrazine was a commercial product, purified following the method reported by Vogel [23].

Azoxybenzene was synthesised according to the procedure reported by Vogel [23].

Nitrobenzene was a commercial product, purified by distillation.

2.2. Hydrogenation experiments

Two typical hydrogenation experiments were reported: the same procedure was employed for all substrates and the data collected on the influence of temperature, hydrogen pressure, catalyst concentration and reaction time are reported in Tables 1–8.

2.2.1. Hydrogenation in the presence of $RuH_2(CO)_2(P^nBu_3)_2$ (1) or $RuH_2(CO)_2(PPh_3)_2$ (2)

The catalyst was prepared immediately before its use from the corresponding acetato complex, following the procedure reported by Salvini et al. [18] for **1** or Frediani et al. [19] for **2**.

In a glass vial inserted in an autoclave $Ru(CO)_2(CH_3COO)_2(PR_3)_2$ (R = ^nBu, Ph) (1.32×10^{-5} mol), 4 mL of anhydrous THF and Na_2CO_3 (5 mmol) were introduced, then hydrogen up to 100 bar was added. The vessel was heated at 100 °C for 14 h in a thermostated oil bath. The reactor was cooled, the gas vented out and the yellow solution filtered and transferred in a Schlenk tube containing azobenzene (1.32 mmol) and p-xylene (160 μl) as internal standard. A further amount of THF was added up to a total volume of 20 mL. The solution was introduced in a high pressure vessel under nitrogen atmosphere, then hydrogen was added up to the pressure required. The vessel was rocked in an oil bath heated at the prefixed temperature, for the time required.

At the end of the reaction the vessel was cooled, the gas vented out and the solution analysed by GC or HPLC and GC–MS techniques.

Table 1
Hydrogenation of azobenzene (**A**) in the presence of $RuH_2(CO)_2(P^nBu_3)_2$ (**1**), $RuH_2(CO)_2(PPh_3)_2$ (**2**), and $RuH_2(PPh_3)_4$ (**3**)

Entry	Category code	T (K)	H_2 (atm)	r.t. (h)	[Catalyst] (mM)	Conversion (%)	Reaction mixture composition (%)		
							A	**B**	**C**
1	**1**	363	50	3	0.66	1.4	98.1	0.8	1.1
2	**1**	383	50	3	0.66	2.8	96.5	2.0	1.5
3	**1**	393	50	3	0.66	4.9	92.3	1.8	5.9
4	**1**	423	50	3	0.66	10.3	82.8	1.8	15.4
5	**1**	393	50	6	0.66	7.3	88.8	2.8	8.4
6	**1**	393	50	9	0.66	15.1	77.9	5.7	16.4
7	**1**	393	50	24	0.66	28.9	57.4	4.1	38.5
8	**1**	393	25	3	0.66	1.8	97.3	0.9	1.8
9	**1**	393	75	3	0.66	13.1	78.2	1.7	20.1
10	**1**	393	50	3	0.23	3.0	95.4	1.4	3.2
11	**1**	393	50	3	1.42	17.3	72.2	2.5	25.3
12	**2**	373	50	3	0.66	1.9	96.9	0.7	2.4
13	**2**	383	50	3	0.66	8.3	87.8	3.7	8.5
14	**2**	393	50	3	0.66	21.9	66.5	3.7	29.8
15	**2**	393	50	6	0.66	26.0	59.4	1.1	39.5
16	**2**	393	50	9	0.66	37.4	46.3	1.6	52.1
17	**2**	393	50	24	0.66	55.9	28.6	1.0	70.4
18	**2**	393	25	3	0.66	4.4	92.4	1.0	6.6
19	**2**	393	35	3	0.66	10.0	82.5	0.9	16.6
20	**2**	393	50	3	0.23	10.2	83.4	2.3	14.3
21	**2**	393	50	3	1.42	35.5	48.3	1.4	50.3
22	**3**	363	50	3	0.66	9.4	87.4	5.6	7.0
23	**3**	373	50	3	0.66	16.1	73.8	2.1	24.1
24	**3**	383	50	3	0.66	26.7	58.9	1.8	39.3
25	**3**	393	50	3	0.66	44.1	40.1	3.3	56.6
26	**3**	393	50	6	0.66	77.5	13.1	2.8	84.1
27	**3**	393	50	9	0.66	87.8	6.9	5.8	87.3
28	**3**	393	50	24	0.66	99.8	0.1	3.7	96.2
29	**3**	393	25	3	0.66	23.6	63.5	2.7	33.8
30	**3**	393	75	3	0.66	49.8	33.5	0.0	66.5
31	**3**	393	100	3	0.66	65.4	21.5	2.9	75.6
32	**3**	393	50	3	0.23	13.5	77.0	1.1	21.9
33	**3**	393	50	3	1.42	59.4	26.4	3.4	70.2

Substrate: 0.066 M; volume of the solution: 20 mL; **A**: azobenzene; **B**: *N,N*-diphenylhydrazine; **C**: aniline.

Table 2
Kinetic and thermodynamic data for the hydrogenation of azobenzene (**A**) in the presence of $RuH_2(CO)_2(P^nBu_3)_2$ (**1**), $RuH_2(CO)_2(PPh_3)_2$ (**2**), and $RuH_2(PPh_3)_4$ (**3**)

Catalyst	$K_c \times 10^6$ (s^{-1})	R^2	$K_p \times 10^7$ ($s^{-1}\ atm^{-1}$)	R^2	$K_{cat} \times 10^4$ ($s^{-1}\ mmol^{-1}\ L$)	R^2	ΔH^{**} ($kJ\ mol^{-1}$)	ΔS^{**} ($J\ mol^{-1}\ K^{-1}$)	R^2
$RuH_2(CO)_2(P^nBu_3)_2$ (**1**)	3.88	0.98	2.25	0.96	1.30	0.94	41.2	−246	1.00
$RuH_2(CO)_2(PPh_3)_2$ (**2**)	7.59	0.98	7.55	0.99	2.55	0.99	151.7	+50	0.98
$RuH_2(PPh_3)_4$ (**3**)	74.7	1.00	9.22	0.93	5.64	0.94	66.7	−159	1.00

Data from Table 1.

Table 3
Hydrogenation of azobenzene (**A**) in the presence of $RuH_2(PPh_3)_4$ (**3**) and a variable amount of free triphenylphosphine

Entry	Free PPh_3 (mM)	Conversion (%) after a reaction time (s) of					
		3600	7200	10 800	21 600	32 400	86 400
34	0	5.1	10.4	11.4	33.0	28.7	97.8
35	1.9	1.4	2.9	1.7	3.7	6.4	34.7
36	11.5	1.3	2.3	3.9	9.8	9.6	32.1

T = 353 K; $p(H_2)$ = 50 atm; $RuH_2(PPh_3)_4$ = 0.66 mM. Volume of the solution 20 mL.

Table 4

Hydrogenolysis of *N,N′*-diphenylhydrazine (**B**) in the presence of RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ (**1**), RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**), and RuH$_2$(PPh$_3$)$_4$ (**3**)

Entry	Category code	T (K)	P atm	r.t. (h)	[Catalyst] (mM)	Conversion (%)	Reaction mixture composition (%)	
							B	**C**
37	**1**	373	50	3	0.66	16.6	71.5	28.5
38	**1**	383	50	3	0.66	19.4	67.5	32.5
39	**1**	393	50	3	0.66	24.3	60.9	39.1
40	**1**	393	50	6	0.66	28.7	55.4	44.6
41	**1**	393	50	9	0.66	34.8	48.4	51.6
42	**1**	393	50	24	0.66	70.1	17.6	82.4
43	**1**	393	25	3	0.66	8.3	84.7	15.3
44	**1**	393	75	3	0.66	33.5	49.8	50.2
45	**1**	393	50	3	0.23	16.1	72.2	27.8
46	**1**	393	50	3	1.42	33.5	49.8	50.2
47	**2**	373	50	3	0.66	41.5	41.3	58.7
48	**2**	383	50	3	0.66	43.0	39.9	60.1
49	**2**	393	50	3	0.66	45.2	37.7	62.3
50	**2**	393	50	6	0.66	48.8	34.4	65.6
51	**2**	393	50	9	0.66	52.8	30.9	69.1
52	**2**	393	50	24	0.66	67.4	19.5	80.5
53	**2**	393	25	3	0.66	18.1	69.4	30.6
54	**2**	393	75	3	0.66	66.9	19.8	80.2
55	**2**	393	50	3	0.23	41.6	41.2	58.8
56	**2**	393	50	3	1.42	53.1	30.6	69.4
57	**3**	373	50	3	0.66	33.3	50.0	50.0
58	**3**	383	50	3	0.66	40.9	41.9	58.1
59	**3**	393	50	3	0.66	46.5	36.5	63.5
60	**3**	393	50	6	0.66	67.1	19.7	80.3
61	**3**	393	50	9	0.66	90.5	5.0	95.0
62	**3**	393	50	24	0.66	97.4	1.3	98.7
63	**3**	393	25	3	0.66	37.6	45.3	54.7
64	**3**	393	75	3	0.66	54.7	29.3	70.7
65	**3**	393	50	3	0.23	18.8	68.4	31.6
66	**3**	393	50	3	1.42	67.4	19.5	80.5

Substrate: 0.066 M; volume of the solution 20 mL; **B**: *N,N*-diphenylhydrazine; **C**: aniline.

Table 5

Kinetic and thermodynamic data from the hydrogenolysis of *N,N′*-diphenylhydrazine (**B**) in the presence of RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ (**1**), RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**), and RuH$_2$(PPh$_3$)$_4$ (**3**)

Ru(II) complexes	$K_c \times 10^5$ (s^{-1})	R^2	$K_p \times 10^7$ (s^{-1} atm^{-1})	R^2	$K_{cat} \times 10^4$ (s^{-1} mmol^{-1} L)	R^2	ΔH^{**} (kJ mol^{-1})	ΔS^{**} (J mol^{-1} K^{-1})	R^2
RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ (**1**)	1.28	0.98	5.96	0.99	3.00	0.99	22.9	−277	1.00
RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**)	0.69	1.00	16.8	1.00	1.73	0.99	3.8	−319	1.00
RuH$_2$(PPh$_3$)$_4$ (**3**)	3.86	0.90	5.91	1.00	6.97	0.99	23.2	−269	1.00

Data from Table 3.

2.2.2. Hydrogenation in the presence of RuH$_2$(PPh$_3$)$_4$ (3) or RuH$_2$[P(OEt$_3$)]$_4$ (4)

In a Schlenk tube RuH$_2$(PR$_3$)$_4$ (R = Ph, OEt) (1.32×10^{-5} mol), substrate (1.32 mmol) and *p*-xylene (160 µl) as internal standard were dissolved in THF (20 mL).

The solution was transferred in a Parr autoclave by suction and, after pressurisation with hydrogen up to the pressure required, the reactor was stirred for the pre-fixed time at the established temperature.

At the end of the reaction the vessel was cooled, the gas vented out and the solution analysed by GC or HPLC and GC–MS techniques.

2.3. Synthesis of new complexes

2.3.1. Reaction of RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ with PhN=NPh

A 1:1 molar solution of RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ and PhN=NPh in C$_6$D$_6$ was introduced in a NMR sample tube and monitored by ^{1}H and ^{31}P NMR. The sample was heated at 373 K for 24 h obtaining a 96% conversion with formation of two new complexes identified as RuH(CO)$_2$(PhN–NHPh)(P^{n}Bu$_3$)$_2$ (**5$_1$**) 61% and Ru-(CO)$_2$(PhNH–NHPh)(P^{n}Bu$_3$)$_2$ (**6$_1$**) 35%. The following characteristic resonances were attributed to the complex **5$_1$**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −10.80 (t, 1H, RuH, J_{HP} 25.1 Hz), 4.82 (s, 1H, NH) ppm; ^{31}P NMR (121

Table 6
Hydrogenation of azoxybenzene (**D**) in the presence of RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**) and RuH$_2$(PPh$_3$)$_4$ (**3**)

Entry	Category code	T (K)	H$_2$ (atm)	r.t. (h)	[Catalyst] (mM)	Conversion (%)	Reaction mixture composition (%)			
							A	**B**	**C**	**(D)**
67	**2**	393	50	9	0.66	53.3	23.3	17.1	16.8	42.8
68	**2**	403	50	9	0.66	65.1	5.0	45.5	17.7	31.8
69	**2**	413	50	9	0.66	70.8	4.7	49.1	19.9	26.3
70	**2**	393	50	3	0.66	42.6	17.3	15.9	13.2	53.6
71	**2**	393	50	15	0.66	55.1	5.1	32.0	23.2	39.7
72	**2**	393	50	24	0.66	65.6	3.9	35.6	31.5	29.0
73	**2**	393	50	48	0.66	100.0	0.0	37.3	62.7	0.0
74	**2**	393	25	9	0.66	21.4	14.4	7.0	0.0	78.6
75	**2**	393	75	9	0.66	53.6	11.9	19.7	28.6	39.8
76	**2**	393	100	9	0.66	63.6	1.1	32.3	36.9	29.7
77	**3**	373	50	6	0.66	55.1	15.9	33.7	7.1	43.3
78	**3**	383	50	6	0.66	63.4	7.7	31.6	29.5	31.2
79	**3**	393	50	6	0.66	69.3	7.4	32.3	35.0	25.3
80	**3**	373	50	3	0.66	44.7	23.9	20.8	0.0	55.3
81	**3**	373	50	9	0.66	62.0	12.0	43.9	7.5	36.6
82	**3**	373	50	24	0.66	100.0	0.0	44.2	55.8	0.0
83	**3**	373	10	6	0.66	39.3	17.2	22.1	0.0	60.7
84	**3**	373	25	6	0.66	49.2	8.8	37.2	4.3	49.7
85	**3**	373	75	6	0.66	64.7	6.8	33.0	30.2	30.0

Substrate: 0.065 M; volume of the solution: 20 mL; **A**: azobenzene; **B**: diphenylhydrazine; **C**: aniline; **D**: azoxybenzene.

Table 7
Kinetic and thermodynamic data for the hydrogenation of azoxybenzene (**D**) in the presence of RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**) and RuH$_2$(PPh$_3$)$_4$ (**3**)

Catalyst	T (K)	$K_c \times 10^6$ (s^{-1})	R^2	T (K)	$K_p \times 10^7$ (s^{-1} atm^{-1})	R^2	ΔH^{**} (kJ mol^{-1})	ΔS^{**} (J mol^{-1} K^{-1})	R^2
RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**)	393	6.37	0.96	393	3.18	1.00	29.0	−262	1.00
RuH$_2$(PPh$_3$)$_4$ (**3**)	373	55.3	1.00	373	3.61	0.98	20.5	−276	1.00

Data from Table 5.

MHz, C$_6$D$_6$, δ) 34.9 ppm. An IR spectrum of the solution shows an absorption at 2931 (v_{NH}) cm^{-1}. The following resonances were attributed to the complex **6$_1$**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) 4.43 (s, 1H, NH) ppm; ^{31}P NMR (121 MHz, C$_6$D$_6$, δ) 33.2 ppm.

2.3.2. Reaction of RuH$_2$(CO)$_2$(PPh$_3$)$_2$ with PhN=NPh

A 1:1 molar solution of RuH$_2$(CO)$_2$(PPh$_3$)$_2$ and PhN=NPh in C$_6$D$_6$ was introduced in a NMR sample tube and monitored by ^{1}H and ^{31}P NMR. The sample was heated at 363 K for 24 h obtaining a 97% conversion with formation of two new complexes identified as RuH(CO)$_2$(PhN–NHPh)(PPh$_3$)$_2$ (**5$_2$**) 78% and Ru-(CO)$_2$(PhNH–NHPh)(PPh$_3$)$_2$ (**6$_2$**) 19%. The following characteristic resonances were attributed to the complex **5$_2$**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −9.70 (t, 1H, RuH, J_{HP} 23.7 Hz) 4.72 (s, 1H, NH) ppm; ^{31}P NMR (121 MHz, C$_6$D$_6$, δ) 56.9 ppm. An IR spectrum of the solution shows an absorption at 2931 (v_{NH}) cm^{-1}. The following resonances were attributed to the complex **6$_2$**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) 4.40 (s, 1H, NH) ppm; ^{31}P NMR (121 MHz, C$_6$D$_6$, δ) 52.4 ppm.

3. Results and discussion

3.1. Hydrogenation of azobenzene (A)

The ruthenium dihydrides **1**–**4** are catalytically active in the hydrogenation of azobenzene (**A**) with molecular hydrogen giving N,N′-diphenylhydrazine (**B**) as intermediate and aniline (**C**) as the final hydrogenation product (Scheme 1). No hydrogenation of the aromatic ring was shown.

3.1.1. Influence of reaction parameters

The influence of several reaction parameters were tested and the results are reported in Table 1.

The complex **3** shows a low activity in the reduction of azobenzene with a 9.4% conversion at 363 K (entry 22) that increases up to 44.1% if the temperature rises to 393 K (entries 22–25) and an almost complete conversion) was reached after 24 h (99.8%, entry 28). Also an increse of hydrogen pressure show a beneficial influence on the conversion which increases from 23.6% up to 65.4% using 25 and 100 atm of hydrogen, respectively (entries 29 and 31). When the catalyst concentration is

Table 8
Hydrogenation of nitrobenzene (**E**) in the presence of RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**) and RuH$_2$(PPh$_3$)$_4$ (**3**)

Entry	Category code	T (K)	H$_2$ (atm)	r.t. (h)	[Catalyst] (mM)	Conversion (%)	Reaction mixture composition (%)	
							C	E
86	**2**	373	50	6	0.66	20.5	20.5	79.5
87	**2**	383	50	6	0.66	25.1	25.1	74.9
88	**2**	393	50	6	0.66	29.7	29.7	70.3
89	**2**	393	50	3	0.66	27.0	27.0	73.0
90	**2**	393	50	8	0.66	33.2	33.2	66.8
91	**2**	393	50	15	0.66	43.1	43.1	56.9
92	**2**	393	50	48	0.66	100.0	100.0	0.0
93	**2**	393	10	6	0.66	24.3	24.3	75.7
94	**2**	393	25	6	0.66	28.3	28.3	71.7
95	**2**	393	75	6	0.66	51.2	51.2	48.8
96	**2**	393	100	6	0.66	59.9	59.9	40.1
97	**3**	363	50	6	0.66	18.1	18.1	81.9
98	**3**	373	50	6	0.66	24.0	24.0	76.0
99	**3**	383	50	6	0.66	50.7	50.7	49.3
100	**3**	393	50	6	0.66	63.1	63.1	36.9
101	**3**	373	50	3	0.66	20.3	20.3	79.7
102	**3**	373	50	9	0.66	27.1	27.1	72.9
103	**3**	373	50	15	0.66	31.6	31.6	68.4
104	**3**	373	50	48	0.66	100.0	100.0	0.0
105	**3**	373	25	6	0.66	19.7	19.7	80.3
106	**3**	373	75	6	0.66	28.1	28.1	71.9
107	**3**	373	100	6	0.66	33.4	33.4	66.6

Substrate: 0.065 M; volume of the solution: 20 mL; **C**: aniline; **E**: nitrobenzene.
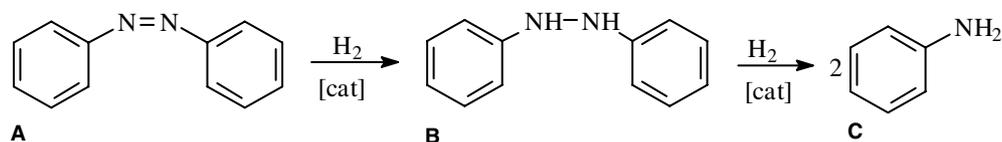
Scheme 1. Hydrogenation of azobenzene.

reduced to 0.23 mM the conversion goes down to 13.5% (entry 32) while it rises to 59.4% if the catalyst concentration is 1.42 m (entry 33).

The catalyst **1** shows a lower activity than **3** and **2**, giving at 363 K only a 1.4% conversion (entry 1, Table 1) that increases up to 10.3% when the temperature rises up to 423 K (entries 1–4), or to 13.1% when the hydrogen pressure increases up to 75 atm (entries 8, 3 and 9) or to 28.9% after 24 h (entry 7). Finally, the conversion increases from 3.0% to 17.3% when the concentration of the catalyst rises from 0.23 up to 1.42 mM (entries 10, 3 and 11).

The hydrogenation of **A** in the presence of **4**, containing two P(OEt)$_3$ ligands, has been performed with low conversion: in the same conditions of entry 25, **4** gives only a 1.4% conversion.

The catalytic activity of the complexes **1–4** is in agreement with their stability. The substitution of two triphenylphosphines with two carbonyl groups in the coordination sphere of the ruthenium catalyst increases the stability but decreases the catalytic activity as shown by the data obtained using **3** or **2** as catalyst. Further-

more, the complex containing two tributylphosphine **1** displays a higher stability than **2**, containing two triphenylphosphine, as shown by their IR spectra in the v_{CO} stretching region and consequently its catalytic activity is lower. Also the substitution of the triphenylphosphine with triethylphosphite as ligand increases the stability of the complex but depress considerably the catalytic activity.

In all hydrogenations the main product is always aniline (**C**) while the amount of the N,N'-diphenylhydrazine (**B**) intermediate does not overcome 5.7%. These results confirm that these catalysts hydrogenate **A**, as reported in Scheme 1, giving **B** as intermediate, and **C** as the final product.

The kinetic of azobenzene hydrogenation in the presence of catalysts **1–3**, have been evaluated following the procedure reported by Salvini et al. [15], using the data reported in Table 1. The reaction rate shows a first partial order with respect to substrate concentration, hydrogen pressure and catalyst concentration. The specific rates are reported in Table 2. The catalyst **3** shows the higher specific rate K_c in the hydrogenation of

azobenzene, an order higher than that obtained in the presence of **2** or **1**. Also the K_p and K_{cat} are in the following order **3 > 2 > 1**.

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**}, evaluated using the Gibbs equation [24] in the temperature range among 363 and 393 K, are reported in Table 2. The positive value of ΔS^{**} (+50 J mol^{-1} K^{-1}) for **2** suggests a dissociative rate determining step. On the contrary, in the presence of **1** and **3** a negative value of ΔS^{**} is obtained (−246 and −159 J mol^{-1} K^{-1}, respectively), suggesting the formation of an intermediate having a higher steric encumbrance than the starting ruthenium complex in the rate determining step.

3.1.2. Mechanism

The catalytic activity is, as above reported, in the following order **3 > 2 ≫ 1 ≫ 4** in agreement with the aptitude of these complexes to dissociate a phosphinic ligand, as previously reported [25]. This dissociation may be required to form the activated substrate containing intermediate as reported in previous results on the hydrogenation of benzonitrile. In that reduction the RuH$_2$(PhCN)(PPh$_3$)$_3$ intermediate was evidenced and spectroscopically characterised [9]. In this hydrogenation an analogous intermediate is not evidenced but we have evaluated that the presence of free phosphine drastically decreases the catalytic activity of **3** (Table 3). For instance working for 24 h at 353 K the hydrogenation of azobenzene goes down from 97.8% in the absence of free phosphine to 32.1% when the concentration of free phosphine is 11.5 mM (Fig. 1).

Taking into account these data the following mechanism is hypothesised (Scheme 2).

In a first step **I**, a phosphine ligand is displaced by azobenzene, according to the above reported catalytic activity and to the first partial order of the reaction rate with respect to substrate and catalyst concentration. This reaction is followed (steps **II** and **III**) by the insertion of azobenzene into a Ru–H bond forming a new complex containing a Ru–N bond RuHL$_2$L$'_2$-(PhNNHPh) (**5**). In the following step **IV** the complex **5** gives the complex RuL$_2$L$'_2$(PhNHNHPh) (**6**) through a hydrogen shift. This last complex reacts with hydrogen giving *N,N'*-diphenylhydrazine (**C**) and restoring the starting complex ready for another catalytic cycle. The first-order reaction rate with respect to hydrogen pressure is in agreement with this last step **V**.

According to this mechanism the presence of free ligand in the reaction medium have a negative effect on step **I**, where a displacement of phosphine is required to coordinate azobenzene.

We have collected evidences on the formation of the complexes **5** and **6** reported in Scheme 4 working in an NMR sample tube and employing the complexes **1** or **2**.

The main spectroscopic data of the new complexes are:

- For RuH(CO)$_2$(PBu$_3$)$_2$(PhNNHPh) (**5$_1$**): ^{1}H NMR (δ) −10.80 (t, 1H, RuH, J_{HP} 25.1 Hz), 4.82 (s, 1H, NH) ppm; ^{31}P NMR (δ) 34.9 ppm, IR (v_{NH}) 2931 cm^{-1}.
- For Ru(CO)$_2$(PBu$_3$)$_2$(PhNHNHPh) (**6$_1$**): ^{1}H NMR (δ) 4.43 (s, 1H, NH) ppm; ^{31}P NMR (δ) 33.2 ppm.
- For RuH(CO)$_2$(PPh$_3$)$_2$(PhNNHPh) (**5$_2$**): ^{1}H NMR (δ) −9.70 (t, 1H, RuH, J_{HP} 23.7 Hz), 4.72 (s, 1H, NH) ppm; ^{31}P NMR (δ) 56.9 ppm, IR (v_{NH}) 2931 cm^{-1}.
- For Ru(CO)$_2$(PPh$_3$)$_2$(PhNHNHPh) (**6$_2$**): ^{1}H NMR (δ) 4.40 (s, 1H, NH) ppm; ^{31}P NMR (δ) 52.4 ppm.

The activation parameters for the hydrogenation of **A** using the three different catalysts (Table 2) suggest a different rate determining step involving the formation of a sterically crowded specie for RuH$_2$(PPh$_3$)$_4$ (**3**) and RuH$_2$(CO)$_2$(P^{n}Bu$_3$)$_2$ (**1**) while a dissociative step is involved for RuH$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**).
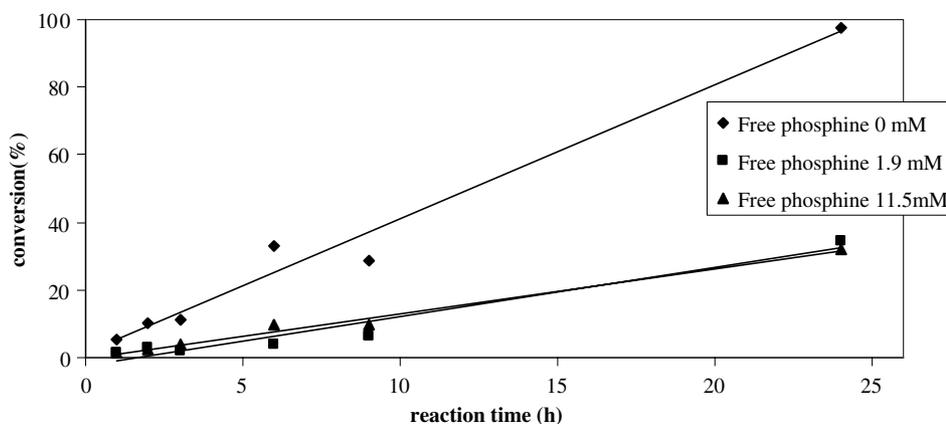

Fig. 1. Hydrogenation of azobenzene (**A**) in the presence of RuH$_2$(PPh$_3$)$_4$ (**3**) and a variable amount of free triphenylphosphine. T = 353 K; p(H$_2$) = 50 atm; RuH$_2$(PPh$_3$)$_4$ 0.66 mM. Volume of the solution 20 mL.

(5_1) L = P^{n}Bu$_3$; L' = CO (6_1) L = P^{n}Bu$_3$; L' = CO

(5_2) L = PPh$_3$; L' = CO (6_2) L = PPh$_3$; L' = CO

(5_3) L = L' = PPh$_3$; (6_3) L = L' = PPh$_3$;
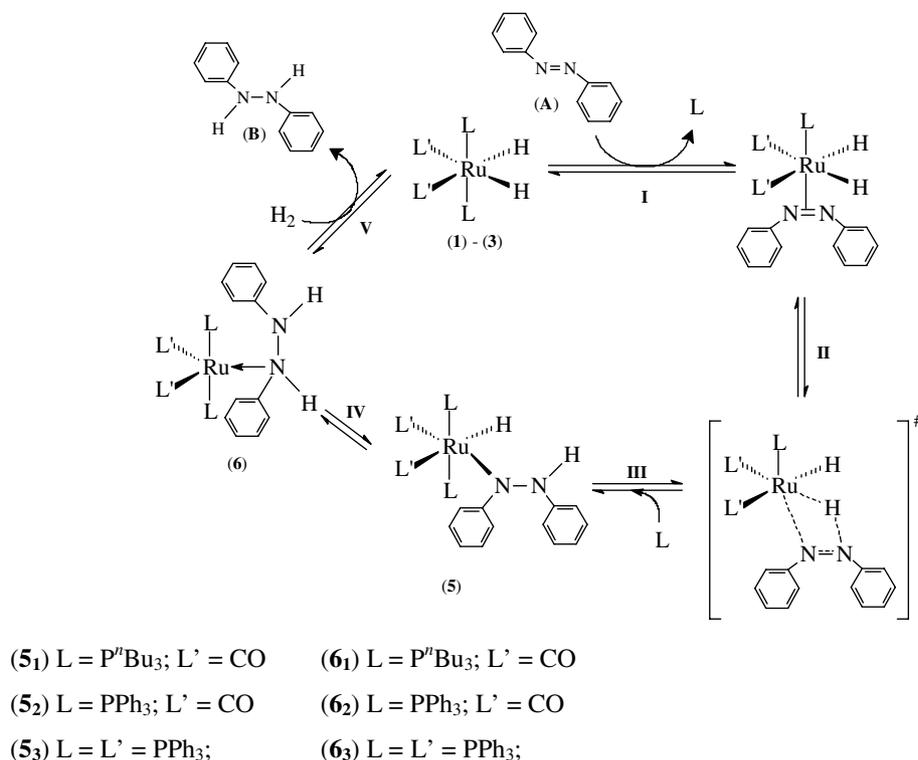
Scheme 2. Suggested mechanism for azobenzene hydrogenation.

The dissociation of the phosphine (step **I**) is very fast, expecially when **3** is the catalyst employed, according to the data reported on the reactivity of these complexes. In the following step **II** a four-centre intermediate is formed followed by the re-insertion of the previously dissociated phosphine (step **III**) to give the complex **5**. In our opinion, in the presence of **1** or **3** as catalyst, the step **III** involving the formation of the complex **5** is the rate determining step, because involves the formation of an intermediate having a high steric encumbrance around the ruthenium. As a consequence a positive activation entropy is required. However, when **2** is the starting ruthenium complex, the rate determining step may be ascribed to the reaction of **6** with hydrogen (step **V**) to give diphenylhydrazine and restore the starting ruthenium complex.

3.2. Hydrogenolysis of N,N'-diphenylhydrazine (B)

N,N'-Diphenylhydrazine is always present among the products of the catalytic hydrogenation of azobenzene (**A**) even if its concentration is low. These data prompted us to study the hydrogenolysis of this product following the procedure above reported for the hydrogenation of azobenzene.

The complexes **1**–**3** are catalytically active in the hydrogenolysis of **B**; the results are reported in Table 4.

Surprisingly, all the catalysts show a lower activity in the hydrogenolysis of **B** than that detected in the hydrogenation of **A**.

The catalyst **3** shows a fairly good activity at 373 K and after 3 h, a 33.3% conversion (entry 57) is shown that increases when hydrogen pressure, temperature and catalyst concentration increase. An almost total conversion of **B** (97.4%) is obtained at 393 K, after 24 h using 50 atm of hydrogen (entry 62).

The catalyst **2** shows in this hydrogenolysis a higher activity than **3** with a conversion of 41.5% at 373 K, however a low increase of the conversion from 41.5% to 45.2% is shown when the temperature rises from 373 to 393 K (entries 47–49), while a strong increases is evidenced when the hydrogen pressure is improved from 25 to 75 atm (conversions from 18.1% to 66.9%, entries 53, 49 and 54) and almost the same conversion (67.4%) was collected in the presence of **2**, after 24 h at 393 K using 50 atm of hydrogen (entry 52).

In the presence of the catalyst **1**, the conversion of **B** is only 16.6% after 3 h at 373 K (entry 37). Increasing the temperature from 373 to 393 K causes a fairly good effect on the conversion that rises from 16.6 to 24.3% (entries 37-39). An analogous beneficial effect has been shown by an increment of hydrogen pressure (entries 43, 39 and 44), or catalyst concentration (entries 45, 39 and 46). Finally, also in the presence of **1** working at 393 K for 24 h under 50 atm of hydrogen a 70.1% conversion of **B** is reached (entry 42).

The data obtained in the hydrogenolysis of **B** are an indication that this substrate is not easily coordinated by the catalysts **1**–**3**. In fact the yields of **C** using **A** as substrate are higher than those obtained when the

intermediate **B** is the starting material. These results suggest that **A** is reduced to give **B** coordinated to ruthenium and this complex, in a large extent, is immediately reduced to **C** while only a small amount of **B** is de-coordinated from the catalyst and, in a following step, it may be slowly activated and transformed into **C**.

The kinetic parameters evaluated using the data reported in Table 4 show a first partial order rate with respect to the concentration of substrate, catalyst and hydrogen pressure (Table 5). Surprisingly, the specific rates with respect to substrate and catalyst concentration are higher for the complex **3** ($K_c = 3.86 \times 10^{-5}$ s^{-1}) than for **2** while the conversions are on the contrary. These data suggest that the starting catalyst **2** is transformed in the course of the reaction in a new catalyst having a low activity. The K_p are almost the same when the catalyst **1** or **3** are employed while a higher value is obtained in the presence of **2**.

The activation parameters evaluated for the three catalysts (Table 5) show negative values of ΔS^{**} suggesting an associative rate determining step in all cases.

A mechanism analogous to that reported in Scheme 2, may be hypothesised for this hydrogenolysis.

3.3. Hydrogenation of azoxybenzene

The catalytic activity of the ruthenium dihydrides **2** and **3**, has been also tested in the hydrogenation of azoxybenzene (**D**), a possible intermediate in the synthesis of azobenzene from nitrobenzene. The catalyst **1** is not tested due to its low ability to hydrogenate **A**.

The reaction gives in a first step azobenzene (**A**) then, according to the data above reported (Section 3.1). *N,N'*-Diphenylhydrazine (**B**) and in the last step aniline (**C**) (Scheme 3).

The influence of several reaction parameters are reported in Table 6.

The complex **3** shows a high activity in the reduction of **D** with a conversion of 62.0% at 373 K after 9 h (entry 81) that rises to a 100% conversion after 24 h (entry 82). Furthermore, **3** is already active with a low pressure of hydrogen (10 atm) giving a conversion of 39.3% after 6 h (entry 83). This value increases up to 64.7% when the hydrogen pressure is 75 atm (entry 85).

The catalyst **2** shows a lower activity than **3** with a conversion of 53.3% working at 393 K (entry 67) that rises to 70.8% at 413 K (entry 69). An increase of the hydrogen pressure from 25 up to 100 atm rises the

conversion from 21.4% to 63.6% at 393 K (entries 74–76) and a complete conversion of **D** is obtained, using **2** as catalyst after 48 h at 393 K (entry 73).

The data obtained confirm that the catalysts **2** and **3** hydrogenate **D** giving **A** and **B** as intermediate, and **C** as the final product (Scheme 3). Aniline (**C**) is the main product when a complete conversion of **D** is reached. On the contrary when the conversion of **D** is low, **C** is not present.

The kinetic of the hydrogenation of azoxybenzene in the presence of catalysts **2**–**3**, shows a first partial order with respect to substrate concentration, and hydrogen pressure. The higher activity of **3** in the hydrogenation of **D**, is in line with the specific rates reported in Table 7.

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**} evaluated using the Gibbs equation [24] (Table 6) show a negative value of ΔS^{**}, suggesting an associative rate determining step in all cases.

The substitution of two carbonyl groups with two triphenylphosphines in the coordination sphere of the ruthenium catalyst increases the catalytic activity as shown by the data obtained in the presence of **2** and **3**.

3.4. Hydrogenation of nitrobenzene

The ruthenium dihydrides **2**–**4** have been also tested as catalysts in the hydrogenation of nitrobenzene (**E**). The complex **1** was not tested due to its low activity in the hydrogenation of **A**. The reaction may give in a first step nitrosobenzene (**F**), then *N*-phenylhydroxylamine (**G**) and in the last step aniline (**C**) (Scheme 4) [26]. The influence of reaction parameters such as temperature, reaction time, and hydrogen pressure are reported in Table 8.

In the presence of **2** an increment of conversion from 20.5% to 29.7% is shown when the temperature rises from 373 up to 393 K (entries 86–88), while increasing hydrogen pressure from 10 up to 100 atm (entries 93–96) at 393 K the conversion rises from 24.3 to 59.9%. The conversion rises also if the reaction time is increased and a complete conversion is reached after 48 h (entry 92).

$$\text{PhNO}_2 \xrightarrow[\text{[Cat]}]{\text{H}_2} \text{PhNO} \xrightarrow[\text{[Cat]}]{\text{H}_2} \text{PhNHOH} \xrightarrow[\text{[Cat]}]{\text{H}_2} \text{PhNH}_2$$

E   **F**   **G**   **C**
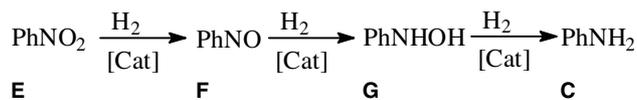
Scheme 4. Hydrogenation of nitrobenzene.

$$\text{Ph}-\overset{\overset{\displaystyle O^-}{\,\shortmid\,}}{\text{N}}=\overset{+}{\text{N}}-\text{Ph} \xrightarrow[\text{[Cat]}]{\text{H}_2} \text{PhN}=\text{NPh} \xrightarrow[\text{[Cat]}]{\text{H}_2} \text{PhNH}-\text{NHPh} \xrightarrow[\text{[Cat]}]{\text{H}_2} 2\,\text{Ph}-\text{NH}_2$$

D   **A**   **B**   **C**
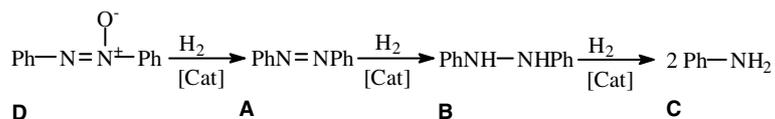
Scheme 3. Hydrogenation of azoxybenzene.

Table 9
Kinetic and thermodynamic data for the hydrogenation of nitrobenzene (E) in the presence of $RuH_2(CO)_2(PPh_3)_2$ (2) and $RuH_2(PPh_3)_4$ (3)

Catalyst	T (K)	$K_c \times 10^6$ (s^{-1})	R^2	T (K)	$K_p \times 10^6$ (s^{-1} atm^{-1})	R^2	ΔH^{**} (kJ mol^{-1})	ΔS^{**} (J mol^{-1} K^{-1})	R^2
$RuH_2(CO)_2(PPh_3)_2$ (2)	393	5.94	0.99	393	3.39	0.90	23.0	−280	1.00
$RuH_2(PPh_3)_4$ (3)	373	3.50	0.99	373	1.23	0.92	30.5	−254	0.95

Data from Table 7.

The complex 3 shows a higher activity than 2 giving a 31.6% conversion after 15 h at 373 K and 50 atm of hydrogen (entry 103) and a complete conversion after 48 h (entry 104). A positive influence on the conversion is shown by an increase of hydrogen pressure and catalyst concentration.

The complex 4 confirms its low catalytic activity in these reductions giving a very poor conversion (2.9%) in the hydrogenation of E in the same condition of entry 89.

In all hydrogenations a complete chemoselectivity towards aniline (C) is obtained; the possible intermediates nitrosobenzene (F) and N-phenylhydroxylamine (G) were never detected. Furthermore, no hydrogenation of the aromatic ring was shown. These data suggest that F and G are easily hydrogenated than E in the presence of 2 or 3 as catalyst.

The hydrogenation of nitrobenzene in the presence of catalysts 2 and 3 show a first partial order with respect to substrate concentration and hydrogen pressure. The catalyst 3 is more active than 2 in the hydrogenation of nitrobenzene, in line with their specific rates (Table 9). In fact almost the same reaction rate is obtained at 373 K in the presence of 3 and at 393 K employing 2 as catalyst. Also the K_p values are in the following order 3 > 2.

The activation parameters ΔG^{**}, ΔS^{**} and ΔH^{**} evaluated using the Gibbs equation [24] show a negative values of ΔS^{**} (−280 J mol^{-1} K^{-1} for 2 and −254 J mol^{-1} K^{-1}, for 3), suggesting an associative rate determining step in all cases.

The data obtained are in agreement with the stability of the ruthenium complexes, as above reported and a mechanism analogous to that reported in Scheme 2 may be hypothesised.

4. Conclusion

The catalysts tested are catalytically active in the hydrogenation of azobenzene (A), azoxybenzene (C) and nitrobenzene (D) and in the hydrogenolysis of diphenylhydrazine (B), even if different activities were shown. The catalyst $RuH_2(PPh_3)_4$ (3) shows a very high activity as shown by the almost complete conversion obtained with all the substrates tested.

A catalytic cycle, analogous to that reported in Scheme 2, may be assumed for the hydrogenation of azobenzene (A), azoxybenzene (D), nitrobenzene (E) and in the hydrogenolysis of diphenylhydrazine (B) in consideration of the analogous kinetic and thermodynamic data collected.

Finally, the data collected on the hydrogenation of A and B suggest that the Ru(N,N'-diphenylhydrazine) complex 6 formed in the hydrogenation of azobenzene (A) or azoxybenzene (D) is further reduced to aniline without dissociation of the coordinated diphenylhydrazine.

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