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Highly Selective Hydrogenation of Carbon–Carbon Multiple Bonds Catalyzed by the Cation $[(C_6Me_6)_2Ru_2(PPh_2)H_2]^+$: Molecular Structure of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$, a Possible Intermediate in the Case of Phenylacetylene Hydrogenation

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Abstract: The dinuclear cation $[(C_6Me_6)_2Ru_2(PPh_2)H_2]^+$ (**1**) has been studied as the catalyst for the hydrogenation of carbon–carbon double and triple bonds. In particular, [**1**][BF_4] turned out to be a highly selective hydrogenation catalyst for olefin functions in molecules also containing reducible carbonyl functions, such as acrolein, carvone, and methyljasmonate. The hypothesis of molecular catalysis by dinuclear ruthenium complexes is supported by catalyst-poisoning experiments, the absence of an induction period in the kinetics of cyclohexene hydrogenation, and the isolation and single-crystal X-ray structure analysis of the tetrafluoroborate salt of the cation $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$ (**2**), which can be considered as an intermediate in the case of phenylacetylene hydrogenation. On the basis of these findings, a catalytic cycle is proposed which implies that substrate hydrogenation takes place at the intact diruthenium backbone, with the two ruthenium atoms acting cooperatively in the hydrogen-transfer process.

Keywords: catalysis · hydrogenation · multiple bonds · ruthenium

Introduction

Over the past three decades, arene ruthenium complexes have been extensively studied,[1] in particular with regard to their catalytic potential for the hydrogenation of unsaturated substrates, such as olefins[2] and ketones.[3] Moreover, the selective hydrogenation of organic molecules plays an important role in the synthesis of fine chemicals through both heterogeneous[4] or homogeneous catalysis,[5] especially as far as selective hydrogenation of carbon–carbon double bonds in unsaturated carbonyl compounds is concerned.[5,6]

The catalytic hydrogenation of unsaturated carbonyl compounds has been the object of numerous investigations[5,6] because, in the case of α,β-unsaturated carbonyl compounds, the chemoselectivity is often low and the catalyst does not tolerate additional functional groups. For example, $[(PPh_3)_3RuCl_2]$, a highly effective catalyst for olefin hydrogenation, was shown to be completely inactive in the hydrogenation of unsaturated aldehydes.[7] Wilkinson's catalyst, $[(PPh_3)_3RhCl]$, which easily decarbonylates aldehydes under mild conditions to give the corresponding hydrocarbon and catalytically inactive $[(PPh_3)_2Rh(CO)Cl]$,[8a] requires a very dilute solution of substrate and pretreatment with H_2 to hydrogenate selectively the C=C bond of unsaturated aldehydes; even under such conditions, Wilkinson's catalyst shows low activity and selectivity, the products often being contaminated with byproducts, such as unsaturated alcohols or hydrocarbons.[8b] Selective C=C hydrogenation in α,β-unsaturated aldehydes and ketones has been reported with $[(PCy_3)_2Rh(H)Cl_2]$ (Cy = cyclohexyl),[9a] palladium nanocomposites,[9b] and organic ammonium salts[9c] as catalysts. With the ternary catalyst systems $[(PPh_3)_3RuCl_2]$/$H_2NCH_2CH_2NH_2$/KOH[10a] and $RuCl_3$/P(*m*$C_6H_4SO_3Na)_3$/H_2O,[10b] the selectivity can be inversed, with the C=O function being reduced preferentially to the C=C function. Recent results and trends in selective catalytic hydrogenation, including enantioselective hydrogenations, are summarized in an extensive review by Blaser et al.[11]

The use of transition-metal complexes is widespread for catalytic hydrogenation reactions. However, the question of

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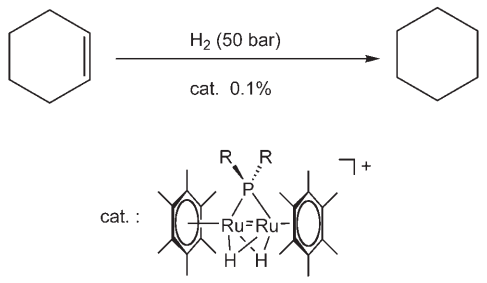
the true nature of the catalyst remains a debatable point, because in situ formation of nanoclusters or metal nanoparticle catalysts seems to be common under reducing conditions.[12] Distinguishing homogeneous catalysis by soluble metal complexes from heterogeneous catalysis by "soluble" metal colloids (nanoparticles) is not trivial.[12] Suitable methods for identifying pseudohomogeneous nanoparticle catalysis, suggested particularly by Lin and Finke, include 1) catalyst recycling studies, 2) kinetics studies, and 3) quantitative catalyst-poisoning experiments.[13] Thus, it was possible to identify Ru^0 nanoclusters as the true catalytic species in the case of benzene hydrogenation catalyzed by $[(C_6Me_6)_2(C_6H_6)Ru_3(O)H_3][BF_4]$ under biphasic conditions,[14a,b] a process initially thought to proceed through an intact trinuclear ruthenium cluster.[14c]

In this paper we report 1) the catalytic activity of the dinuclear arene ruthenium complex $[(C_6Me_6)_2Ru_2(PPh_2)H_2]^+$ (**1**) and derivatives thereof for the catalytic hydrogenation of cyclohexene, 2) a mechanistic study of the catalytic process, in particular, through catalyst recycling, kinetics, and catalyst-poisoning experiments, 3) the catalytic hydrogenation of other olefins and of acetylenes with the isolation and characterization of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H][BF_4]$ ([**2**][BF_4]), a possible catalytic intermediate in the case of phenylacetylene hydrogenation, and 4) the high selectivity of [**1**][BF_4] for olefin hydrogenation in various unsaturated carbonyl compounds.

Results and Discussion

Recently we found that $[(C_6Me_6)_2Ru_2H_3]^+$[15] reacts with thiophenols (RSH) to give complexes of the type $[(C_6Me_6)_2Ru_2(SR)_2H]^+$, building blocks for organometallic conjugated oligomers,[16] and with disubstituted (PR_2H) or trisubstituted (PR_3) phosphanes to give, through P–H or P–C bond cleavage, respectively, complexes of the type $[(C_6Me_6)_2Ru_2(PR_2)H_2]^+$ (**1**: R = Ph, **3**: R = Me, **4**: R = *n*Bu, **5**: R = *t*Bu), which can be isolated as their tetrafluoroborate salts.[1j]

All of the phosphido-bridged arene ruthenium complexes **1**–**5** are more or less active for the catalytic hydrogenation of cyclohexene (Scheme 1). For this catalytic hydrogenation reaction, we used a substrate/catalyst ratio of 1000:1 in ethanol and the reaction was carried out at a hydrogen pressure of 50 bar. The catalytic activities of compounds [**1**][BF_4] (R = Ph), [**3**][BF_4] (R = Me), [**4**][BF_4] (R = *n*Bu), and [**5**][BF_4] (R = *t*Bu) are summarized in Table 1.



Scheme 1. Catalytic hydrogenation of cyclohexene to cyclohexane.

Table 1. Catalytic activity of the complexes in cyclohexene hydrogenation.[a]

Catalyst	*t* [h]	Yield [%][b]	TON[c]	TOF [h^{-1}][d]
[**1**][BF_4]	24	95	950	40
[**3**][BF_4]	24	2	20	0.8
[**4**][BF_4]	24	45	450	19
[**5**][BF_4]	24	5	50	2

[a] Conditions: catalyst/cyclohexene ratio = 1:1000, 50 bar, 40 °C. [b] Yield as determined by GC analysis. [c] Turnover number (TON) = mol of cyclohexane per mol of catalyst. [d] Turnover frequency (TOF) = mol of cyclohexane per mol of catalyst per hour.

The phenyl derivative [**1**][BF_4] is the most active catalyst of this series. The low activity of the *tert*-butyl derivative [**5**][BF_4] may be explained by the steric hindrance of the *tert*-butyl substituents at the phosphorus atom, which forces the arene moieties to adopt a tilted geometry, thereby preventing the substrate from approaching the "metal-hydride" center. However, this is not the only effect that influences the activity, because the methyl derivative [**3**][BF_4], which possesses less bulky substituents at the phosphorus atom, shows the lowest activity. The electronic effects of the substituents also modify the catalytic activity of this type of complex.

In all of these cases, the catalyst is recovered intact, as determined by ^{1}H NMR and MS analysis, at least to more than 90% after a catalytic run. As one of "Halpern's rules" says that "if you can isolate it, it is probably not the catalyst", we decided to investigate the mechanistic aspects of this catalytic reaction with [**1**][BF_4] by Finke's method[12,13] by studying catalyst recycling and reproducibility, the kinetics of the reaction, and by catalyst-poisoning experiments with Hg^0 or strong coordinating ligands, such as 1,10-phenanthroline[14a] and triphenylphosphane.[17]

Catalyst-recycling and reproducibility studies: Pure [**1**][BF_4] was used to hydrogenate cyclohexene at 50 bar H_2 and 40 °C in ethanol. The main product recovered after the catalytic reaction (more than 90%) was intact [**1**][BF_4], according to ^{1}H NMR and MS analysis. No metallic film or metal particles were observed on the wall of the glass vessel, on the magnetic stirrer, or in the catalytic solution. As shown in Table 2, the catalytic activity of [**1**][BF_4] slightly decreases from one run to another. After the first catalytic run, the

Table 2. Recycling catalyst and reproducibility tests.[a]

Run	Catalyst	Substrate/catalyst ratio	TON[b]	TOF [h^{-1}]
1	[**1**][BF_4]	2000:1	1400	58
2	residue of run 1		1240	51
3	residue of run 2		1140	47

[a] Conditions: 50 bar, 40 °C, 24 h. [b] TON as determined by GC analysis.

catalyst is recovered intact, as confirmed by ^{1}H NMR and MS analysis of the complex, but a second diruthenium complex can be detected by MS of the catalytic solution after the second run (ESI MS: $m/z = 749$, while [**1**][BF_4] shows a peak at $m/z = 715$ $[M+H]^+$). After the third catalytic run, this product cannot only be detected by mass spectrometry but also by ^{1}H NMR spectroscopy (200 MHz, [D_6]acetone, 25 °C: $\delta = 7.70$–7.50 (m; CH of phenyl), 7.0–6.8 (m; CH of phenyl), 2.19 (s; $C_6(CH_3)_6$), −12.10 ppm (d, $^2J(H,P) = 39$ Hz; hydride)). It seems to have the same structural features as **1**, but so far it has not been possible to isolate and characterize it.

Kinetic study: Figure 1 shows the kinetic curve for the cyclohexene hydrogenation reaction with [**1**][BF_4]. As the cyclohexene conversion with time does not show an induction

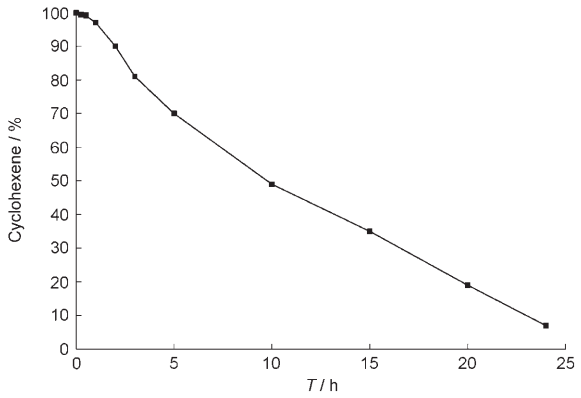


Figure 1. Kinetic study for cyclohexene hydrogenation with [**1**][BF_4]. Conditions: catalyst/substrate ratio = 1:1000, 50 bar, 40 °C (preheated at 40 °C for 2 h before pressurization). The reaction was stopped after the desired time and the rate of cyclohexane formation was determined by GC analysis.

period, if the reaction mixture containing the catalyst is preheated to 40 °C prior to pressurization with hydrogen, it is likely that **1** is indeed the true catalyst, at least under these mild conditions. This is distinctly different from the case of benzene hydrogenation with molecular ruthenium precursors, such as $[(C_6Me_6)_2(C_6H_6)Ru_3(O)H_3]^+$, for which the kinetic curve shows a sigmoidal behavior with a long induction period, a result that is indicative of catalysis by Ru^0 nanoclusters formed from the molecular precursor under the (reductive) catalytic conditions.[14a]

To determine the rate law for the catalytic hydrogenation of cyclohexene with [**1**][BF_4], we performed the catalytic hydrogenation of cyclohexene with different catalyst concentrations. Figure 2 shows typical time courses of the cyclohexene hydrogenation as a function of three different concentrations of [**1**][BF_4]. The hydrogenation rate was determined from the slope of the linear trace, with hydrogenation occurring in the range of low conversion of cyclohexene and hydrogen.

Surprisingly, the hydrogenation of cyclohexene was not found to be first order with respect to the concentration of

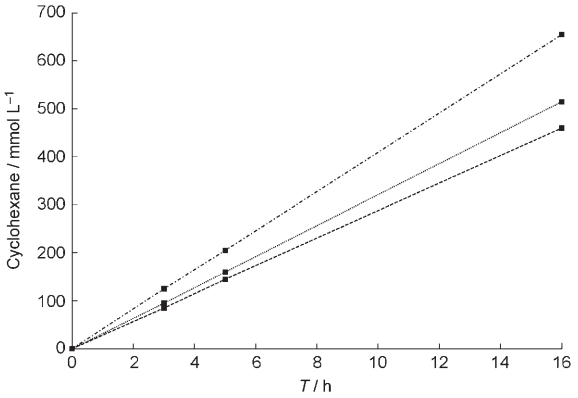


Figure 2. Kinetics of the cyclohexene hydrogenation with different concentrations of [**1**][BF_4]. Conditions: cyclohexene (0.1 mol, 10 mL), 50 bar, 40 °C (preheated at 40 °C for 2 h before pressurization). [**1**][BF_4] (4, 12, or 20 mg) was dissolved in ethanol (10 mL). The reaction was stopped after the desired time and the rate of cyclohexane formation was determined by GC analysis. Catalyst = 0.25 mmol L^{-1} (-----), catalyst = 0.75 mmol L^{-1} (•••••), catalyst = 1.25 mmol L^{-1} (–•–•).

[**1**][BF_4], as would be expected if **1** were the catalytically active species and if the addition of cyclohexene to **1** was the rate-determining step. In this case, the trace in Figure 3 would have been a straight line (linear dependence of the reaction rate on the catalyst concentration).

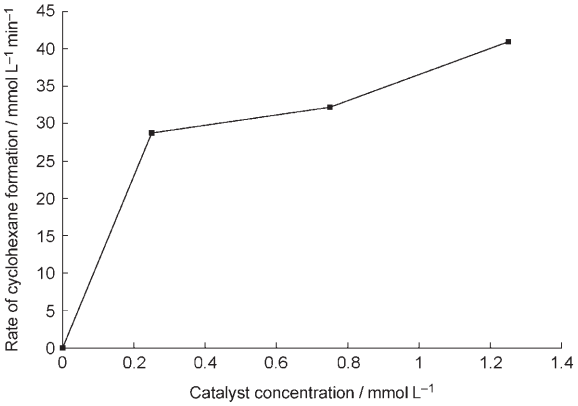


Figure 3. Rate of catalytic hydrogenation of cyclohexene as a function of [**1**][BF_4] concentration.

A possible explanation for the deviation from first-order kinetics could be the limited solubility of hydrogen in ethanol (0.378 g L^{-1} at 18 °C, 50 bar),[18] in which case the kinetics of the catalytic reaction could be determined by mass-transport limitations. In accordance with this assumption, we observed that the reaction rate is strongly dependent on the stirring rate. In fact, under identical conditions (40 °C, 50 bar, 16 h), the cyclohexane conversion of 10 % for the usual stirring rate of ≈500 rpm can be increased to 13 % with a stirring rate of ≈1000 rpm and it drops to only 3 % for a stirring rate of 0 rpm.

We also tried other solvents, such as THF, dichloromethane, acetone, methanol, and isopropanol for this reaction.

The best results were obtained with alcohols, the differences between methanol, ethanol, and isopropanol being very small.

Catalyst-poisoning experiments: To exclude catalysis by metallic species, such as Ru^0 nanoclusters or colloids formed from a molecular precursor under the catalytic conditions, we carried out the catalytic reaction with [**1**][BF_4] in the presence of metallic mercury, 1,10-phenanthroline, or triphenylphosphane. Metallic mercury is known to deactivate metallic ruthenium by amalgamation, while strong ligands, such as 1,10-phenanthroline or triphenylphosphane deactivate metallic ruthenium by complexation.[12,13] The Hg^0-poisoning experiment was carried out by adding ≈400 equivalents of Hg^0 (with respect to the catalyst) to a solution containing the catalyst and the substrate at the beginning of the reaction; the reaction was then performed as usual (see the Experimental Section) with the metallic mercury being present during the whole reaction. The cyclohexene conversion was determined after 24 h of reaction. The same procedure was used for the 1,10-phenanthroline and triphenylphosphane-poisoning experiments, but in these cases only two equivalents of poison (with respect to the catalyst) were added to the solution (Table 3). In addition, we also performed a kinetic study in the presence of Hg^0 during the first three hours of the reaction to compare the conversion rate of cyclohexene in the presence or absence of mercury (Figure 4).

Table 3. Catalyst-poisoning experiments.[a]

Catalyst	Poison	Poison/ catalyst ratio	Yield[b] [%]	Activity loss [%][c]
[**1**][BF_4]	mercury	400:1	30	65
[**1**][BF_4]	triphenylphosphane	2:1	63	32
[**1**][BF_4]	1,10-phenanthroline	2:1	78	17

[a] Conditions: catalyst/cyclohexene ratio = 1:1000, 50 bar, 40 °C, 24 h. [b] Yield as determined by GC analysis. [c] Compared to the activity of [**1**][BF_4] in Table 1.

In the case of strong ligand poisoning, it is known that if less than one equivalent of poison (with respect to the metal atoms), inhibits the catalytic reaction this is indicative of heterogeneous catalysis, in which ≪100% (and often <50%) of the metal atoms are on the metal-particle surface and thus <50% are available to the added poisons.[12,13] In the case of **1**, addition of one equivalent of 1,10-phenanthroline or triphenylphosphane per ruthenium atom (two equivalents per complex **1**) does not significantly affect the activity of the catalyst; the activity loss is only 32% in the case of triphenylphosphane and only 17% for 1,10-phenanthroline (Table 3). This slight activity loss can be explained by competition between the poison molecule and the substrate molecule in the interaction with complex **1**.

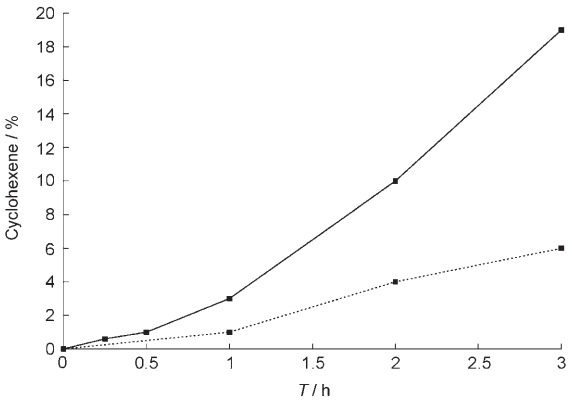


Figure 4. Kinetics of cyclohexene hydrogenation catalyzed by [**1**][BF_4] in the presence or absence of Hg^0. Without Hg^0 (——), with Hg^0 (-----).

In the case of mercury poisoning, the addition of even 200 equivalents of Hg^0 per ruthenium atom does not completely inhibit the catalytic reaction. The activity loss of 65% may be due to adsorption of cation **1** at the mercury surface. The kinetics in the presence and absence of mercury (200 equivalents) demonstrate that the reaction rate does not drop immediately upon mercury addition but slows down slowly with time (Figure 4).

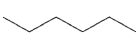
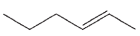
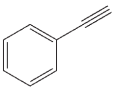
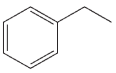
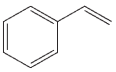
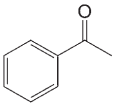
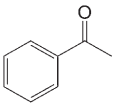
Catalytic hydrogenation potential of [1][BF_4]: The water-tolerant cation **1** was tested as a catalyst for the hydrogenation of unsaturated substrates (olefins, alkynes, ketones, arenes) in ethanol under a 50 bar pressure of hydrogen at 40 or 60 °C. The results, which are summarized in Table 4, show that C=C functions are easily hydrogenated, while C≡C functions are hydrogenated under more forcing conditions and C=O functions and aromatic systems are not converted at all.

The catalyst shows moderate activity for the catalytic hydrogenation of olefins, as compared to efficient catalysts, such as [$Ru(PPh_3)_3Cl_2$][7] or [$Rh(PPh_3)_3Cl$] (Wilkinson's catalyst).[8b] As a general rule, the catalytic activity of homogeneous catalysts decreases in the series $RHC{=}CH_2 > cyclohexene > R_2C{=}CH_2 > RHC{=}CHR > R_2C{=}CHR > R_2C{=}CR_2$ with the increasing steric bulk at the double bond.[19] For this reason, **1** is slightly more active for the hydrogenation of 1-hexene (TOF = 69 h^{-1}, Table 4) than for cyclohexene (TOF = 58 h^{-1}, Table 2) under the same experimental conditions. In the case of 1-hexene hydrogenation, some 2-hexene is also formed as a side product; however, the *E*/*Z* ratio has not been determined.

Cation **1** is less active for C≡C bonds: More than 60% phenylacetylene is recovered unchanged, even if the reaction is carried out at 60 instead of 40 °C. In addition, the selectivity of **1** is not very high. While the main hydrogenation product (60 °C, 24 h) of phenylacetylene is styrene (24%), ethylbenzene is also formed (10%). However, with reduced catalytic activity there is a chance of isolating products from the reaction of [**1**][BF_4] with phenylacetylene that may be intermediates in the catalytic hydrogenation reaction.

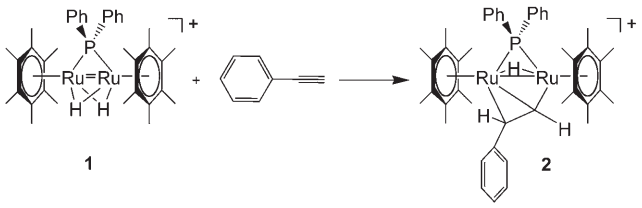
Reaction of [1][BF_4] with phenylacetylene: In the catalytic hydrogenation of phenylacetylene, [**1**][BF_4] is not recovered intact as it is with olefin substrates. A mass spectrometry analysis of the crude catalytic solution reveals that **1** (*m*/*z* =

Table 4. Catalytic hydrogenation of various functions with [**1**][BF_4].

Substrate	t [h]	T [°C]	Substrate/catalyst ratio	Products	TON	TOF [h^{-1}]
	24	40	1000:1		950[a]	40
	24	40	2000:1		1660[b]	69
					340[b]	14
	24	60	1000:1		100[a]	4
					240[a]	10
	24	60	1000:1		0[a]	0

[a] TON as determined by GC analysis. [b] TON as determined by ^{1}H NMR spectroscopy.

713) has disappeared, but a new organometallic complex ($m/z = 816$) showing the characteristic Ru_2 isotope pattern has been formed, among other organometallic species, and this could be a possible intermediate in the catalytic process. To isolate this complex in reasonable yield, we mixed [**1**][BF_4] and phenylacetylene at 60 °C in ethanol without hydrogen pressurization. After purification by thin-layer chromatography, a pure brown-green product [**2**][BF_4] was isolated in 30 % yield and characterized (Scheme 2).



Scheme 2. Synthesis of the dinuclear cation $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$ (**2**).

Brown crystals of [**2**][BF_4] suitable for X-ray analysis were obtained by diffusion of hexane in an acetone solution of the complex. The single-crystal X-ray-structure analysis of cation **2** reveals a bridging styrenyl ligand coordinated to the two ruthenium atoms, with each ruthenium atom being coordinated to a η^6-C_6Me_6 ligand. The formation of this styrenyl ligand can be explained by the insertion of the C≡C unit of phenylacetylene into one of the two Ru–H–Ru bridges. The molecular structure of **2** is shown in Figure 5.

The Ru–Ru distance [2.7923(6) Å] is in the range of a ruthenium–ruthenium single bond. However, it is slightly shorter than those observed in the analogous complexes $[Ru_2(CO)_4(CHCHPh)(dppm)_2][BF_4]$ (dppm = bis(diphenylphosphino)methane)[20a] and $[\{(C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_3(CHCHPh)][BF_4]$.[20b] The presence of PPh_2 and styrene bridging ligands forces the arene moieties to adopt a tilted geometry. The two C_6Me_6 arene ligands are not parallel to each other and the angle between the C_6Me_6 planes is 48.00(14)°. The two hydrogen atoms at the C=C bond of the styrene ligand have a *trans* configuration to each other.

Mechanistic proposal: To find out if **2**, formed during the catalytic hydrogenation of phenylacetylene catalyzed by **1**, really is an intermediate in the catalytic cycle, we treated the isolated [**2**][BF_4] in ethanol with hydrogen under conditions comparable to the catalytic reaction (50 bar, 60 °C, 24 h). We observed the formation of styrene and of **1**, isolated as [**1**][BF_4] in 10 % yield (Scheme 3). Unidentified organome-

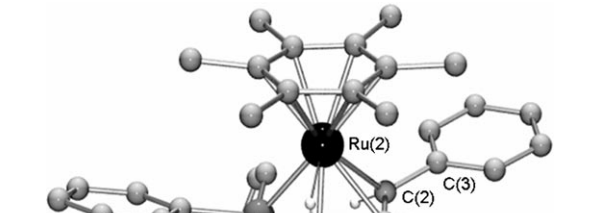
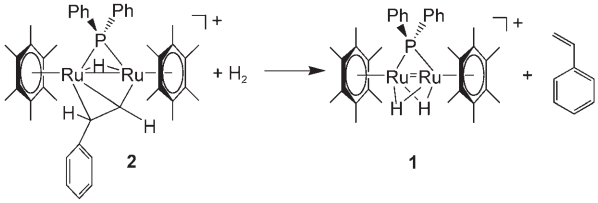


Figure 5. Molecular structure of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$ (**2**); the hydrogen atoms and tetrafluoroborate molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7923(6), Ru(1)–P(1) 2.2900(9), Ru(2)–P(1) 2.3171(11), Ru(1)–C(1) 2.032(4), Ru(2)–C(1) 2.180(4), Ru(2)–C(2) 2.387(4), C(1)–C(2) 1.374(6); Ru(1)-P(1)-Ru(2) 74.61(3), Ru(1)-C(1)-Ru(2) 82.97(16), Ru(1)-C(1)-C(2) 128.7(3), C(1)-C(2)-C(3) 126.1(3).

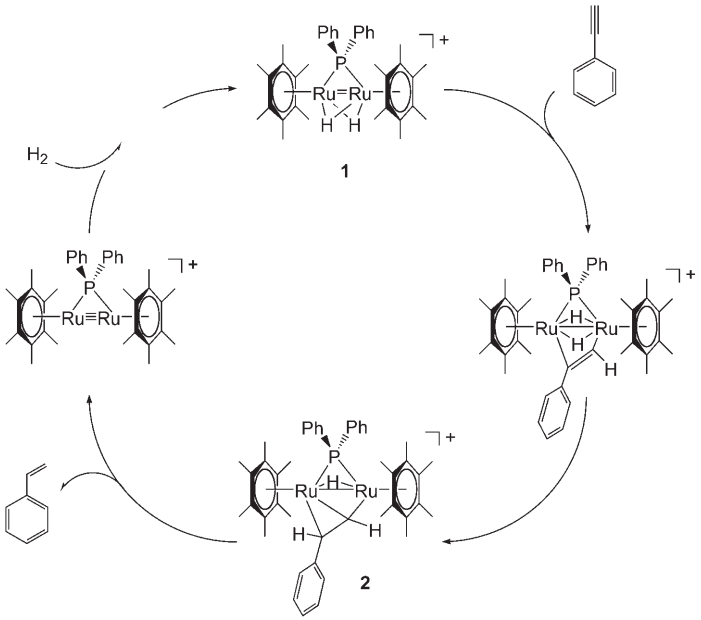


Scheme 3. Conversion of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$ (**2**) under H_2 pressure (50 bar, 60 °C, 24 h) into $[(C_6Me_6)_2Ru_2(PPh_2)H_2]^+$ (**1**).

tallic species were also formed; however, most of the organometallic residue is unreacted **2**.

An unidentified side product, formed in low yield in the conversion of **2** into **1** under H_2 pressure, shows a hydride resonance at $\delta = -13.97$ ppm (d, $^2J(H,P) = 37$ Hz) in the ^1H NMR spectrum of the reaction mixture. This side product is also present in small amounts in the reaction mixture of the phenylacetylene hydrogenation catalyzed by **1**, for which the ^1H NMR spectrum of the reaction mixture shows the same hydride signal at $\delta = -13.97$ ppm, apart from the hydride signal of **2** at $\delta = -18.91$ ppm (dd, $^2J(H,P) = 20$ Hz, $^3J(H,H) = 5.6$ Hz). Due to the small amount of this side product, it has not been identified so far; it may be a deactivated product of **1** or **2** formed during the forcing conditions of phenylacetylene hydrogenation.

A tentative catalytic cycle for the hydrogenation of phenylacetylene in the presence of [**1**][BF_4], based on the isolation of [**2**][BF_4] and its reconversion into [**1**][BF_4] under hydrogen pressurization, is shown in Scheme 4.



Scheme 4. Tentative catalytic cycle for the hydrogenation of phenylacetylene catalyzed by **1**.

In this tentative mechanism, it is assumed that phenylacetylene coordinates to **1** as a μ_2–η^2 ligand with the π system of the carbon–carbon bond; this is followed by transfer of one of the two hydrido ligands from the metal backbone to the internal carbon atom of the π ligand to give **2**, which can be isolated as [**2**][BF_4]. Transfer of the second hydrido ligand from the diruthenium unit to the terminal carbon atom of the π ligand liberates the catalytic product, styrene, and leads to an unsaturated diruthenium complex with a formal metal–metal triple bond, which is thought to react with H_2 to give **1**.

A similar mechanism for the hydrogenation of diphenylacetylene, catalyzed by a dinuclear iridium complex, has been proposed by Oro and co-workers.[21] The difference, however, in their proposal is the coordination of the alkyne ligand to one metal center,[21] whereas in **2** the alkyne has inserted into a bridging hydride and coordinates to both metal centers. Duckett, Dyson, and co-workers have shown that with parahydrogen, for catalytic hydrogenation reactions with ruthenium clusters, polar solvents favor the catalytic reaction taking place at the intact ruthenium backbone, whereas unpolar solvents favor fragmentation to give mononuclear intermediates.[19]

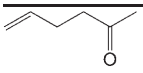
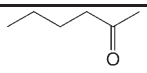
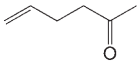
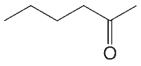
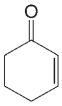
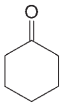
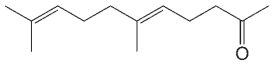
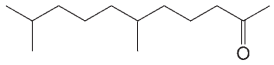
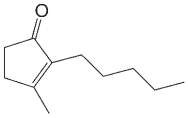
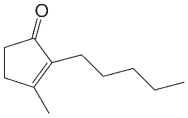
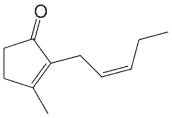
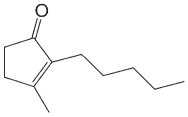
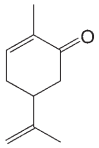
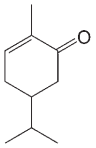
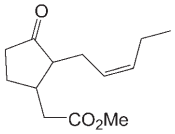
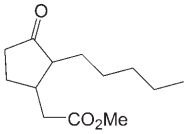
Selective hydrogenation of unsaturated carbonyl compounds: Ruthenium complexes are often used for chemoselective hydrogenation reactions[22] because they are, in general, less active for hydrogenation than rhodium or iridium complexes. As the carbonyl function of ketones is not reduced by [**1**][BF_4] under hydrogen pressurization, we investigated the hydrogenation selectivity of this catalyst with organic molecules that contain both C=C and C=O bonds, such as carvone, *cis*-jasmone, methyljasmonate, or geranylacetone.

As demonstrated by the results summarized in Table 5, [**1**][BF_4] specifically catalyzes the hydrogenation of the C=C bonds in unsaturated aldehydes or ketones, while the C=O bond is not reduced at all. Thus, the reaction of hex-5-en-2-one yields 85% of hexan-2-one after 24 h at 60°C in a very clean reaction. The missing 15% is unreacted starting material and no trace of hexan-2-ol was detected by NMR spectroscopy or GC analysis. However, as compared to the results with unfunctionalized olefins, the catalytic activity of [**1**][BF_4] is lower for olefins containing a carbonyl function, particularly in the case of C=C and C=O conjugation (α,β-unsaturated aldehydes and ketones). In the case of cyclohex-2-en-1-one, [**1**][BF_4] is less active (TON = 20 after 24 h) than the rhodium complex [$(PCy_3)_2Rh(H)Cl_2$] (TON = 192 after 11 h).[9a] If the substrate contains more than one C=C bond as well as a C=O bond, both C=C bonds are hydrogenated without reduction of the C=O function. Thus, geranylacetone gives 85% of tetrahydrogeranylacetone after 24 h at 60°C (TON = 85). In *cis*-jasmone, the nonconjugated exocyclic C=C bond is regiospecifically reduced to give exclusively dihydro-*cis*-jasmone (47% conversion after 24 h at 60°C). Similarly, the hydrogenation of methyljasmonate gives exclusively dihydromethyljasmonate (conversion 90%), a large-volume perfumery chemical, in the presence of [**1**]-[BF_4] (1:100, 50 bar, 60°C, 24 h).[23]

Conclusion

The present study reveals the dinuclear complex $[(C_6Me_6)_2Ru_2(PPh_2)H_2]^+$ (**1**) to be a highly selective hydrogenation catalyst for carbon–carbon multiple bonds in complex molecules containing other reducible functions. The isolation and single-crystal X-ray-structure analysis of the tetrafluoroborate salt of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H]^+$ (**2**), formed from **1** and phenylacetylene, suggest that the catalyt-

Table 5. Catalytic hydrogenation of an olefin in various unsaturated carbonyl compounds.[a]

Substrate	t [h]	T [°C]	Substrate/catalyst ratio	Product	Yield [%]	TON
	144	40	1000:1		63	630[b]
	24	60	100:1		85	85[b]
	24	60	100:1		30	30[b]
	24	60	100:1		20	20[b]
	24	60	100:1		85	85[c]
	24	60 or 80	100:1		0	0[c]
	24	60	100:1		47	47[c]
	24	60	100:1		34	34[c]
	24	60	100:1		90	90[c]

[a] Conditions: 50 bar, EtOH (3 mL). [b] TON as determined by GC analysis. [c] TON as determined by ^{1}H and ^{13}C NMR spectroscopy.

ic hydrogenation proceeds at the diruthenium backbone. Kinetic and poisoning experiments support the hypothesis of molecular catalysis within the coordination sphere of the dinuclear $(C_6Me_6)_2Ru_2(PPh_2)$ moiety.

Experimental Section

General: Solvents (puriss., pa.) were degassed and saturated with nitrogen prior to use. All manipulations were carried out under nitrogen by using standard Schlenk techniques. The dinuclear complexes $[(C_6Me_6)_2Ru_2(PR_2)H_2]^+$ (**1**: R = Ph, **3**: R = Me, **4**: R = *n*Bu, **5**: R = *t*Bu), isolated as their tetrafluoroborate salts, were synthesized as previously described.[1j] All reagents were purchased from Aldrich or Fluka and used as received. Silica gel (type G) used for preparative thin-layer chromatography was purchased from Macherey Nagel GmbH. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, NMR spectra were recorded by using a Bruker 400 MHz or Varian-Gemini 200 MHz spectrometer. ESI mass spectra were recorded at the University of Fribourg by Prof. Titus Jenny. Microanalyses were carried out at the Laboratory of Pharmaceutical Chemistry, University of Geneva.

Synthesis of $[(C_6Me_6)_2Ru_2(PPh_2)(CHCHPh)H][BF_4]$ ([2][BF$_4$]): Phenylacetylene (56 μL, 51.6 mg, 0.504 mmol) was added to a solution of [**1**][BF$_4$] (100 mg, 0.125 mmol) in ethanol (20 mL) under nitrogen at room temperature in a pressure Schlenk tube. The resulting solution was heated to 60 °C and stirred for 20 h. After 20 h, the reaction mixture was cooled to room temperature and the solvent was evaporated to dryness. The crude product was washed with diethyl ether (3 × 20 mL) and then the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluent: acetone/dichloromethane 1:10). The fraction containing the product was extracted with acetone from the green-brown band, which was in front of the main brown band containing [**1**][BF$_4$]. Evaporation of the solvent gave the pure product (yield 30 %): ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 8.38 (dd, ^3J(H,H) = 6.4, ^4J(H,H) = 3.5 Hz, 1H; *H*-Ar), 7.54–6.95 (m, 13H, *H*-Ar), 6.47 (dd, ^3J(H,H) = 6.4, ^4J(H,H) = 3.5 Hz, 1H; *H*-Ar), 3.13 (dd, ^3J(H,P) = 29, ^3J(H,H) = 6 Hz, 1H; *H*C=CH), 2.75 (m, 1H; CH=C*H*), 2.02 (m, 36H; C$_6$-(C*H*$_3$)$_6$), −18.91 ppm (dd, ^2J(H,P) = 20 Hz, ^3J(H,H) = 5.6 Hz, 1H; hydride); ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 151.47 (C_6H_5–CH=C), 135.99 (C_6H_5–CH=C), 135.26 (P(C_6H_5)$_2$), 135.15 (P(C_6H_5)$_2$), 134.24 (C_6H_5–CH=C), 132.83 (P(C_6H_5)$_2$), 132.75 (P(C_6H_5)$_2$), 131.33 (C_6H_5–CH=C), 130.70 (C_6H_5–CH=C), 130.25 (C_6H_5–CH=C), 129.53 (C_6H_5–CH=C), 128.92 (P(C_6H_5)$_2$), 128.82 (P(C_6H_5)$_2$), 127.82 (P(C_6H_5)$_2$), 127.73 (P-(C_6H_5)$_2$), 121.97 (C_6H_5–CH=*C*), 104.67 (C_6(CH$_3$)$_6$), 96.25 (C_6(CH$_3$)$_6$), 16.68 (C_6(*C*H$_3$)$_6$), 15.98 ppm (C_6(*C*H$_3$)$_6$); ^{31}P{^{1}H} NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = 50.18 (d, ^2J(H,P) = 20 Hz); MS (ESI): m/z: 817 $[M+H]^+$; elemental analysis calcd (%) for $C_{44}H_{54}BF_4PRu_2$ (902.82): C 58.54, H 6.03; found: C 58.73, H 6.12.

Catalytic runs: In a typical experiment, $[(C_6Me_6)_2Ru_2(PPh_2)H_2][BF_4]$ ([**1**][BF$_4$]; 8 mg, 0.01 mmol) was dissolved in degassed ethanol (10 mL) in a glass tube (diameter = 20 mm, height = 165 mm). The required amount of substrate was then added to the solution. After the tube was purged four times with hydrogen, the autoclave was pressurized with hydrogen (50 bar) and heated to 40 °C. After 24 h, the autoclave was cooled to

room temperature and the pressure was released. The resulting solution was analyzed by GC analysis.

Other catalytic runs were performed in the same way under the conditions specified in the appropriate tables.

X-ray crystallographic study of [2][BF_4]: $C_{44}H_{54}BF_4PRu_2$, M = 902.79 g mol^{-1}, orthorhombic, $Pna2_1$ (no. 33), a = 19.455(4), b = 10.823(2), c = 18.805(4) Å, V = 3959.6(14) Å^3, T = 203 K, Z = 4, $\mu(Mo_{K\alpha})$ = 0.853 mm^{-1}, 12579 reflections measured, 5769 unique (R_{int} = 0.0441), which were used in all calculations. The final wR (F^2) value was 0.0504 (all data). The data were measured with a Stoe Image Plate Diffraction system equipped with a ϕ circle, by using $Mo_{K\alpha}$ graphite-monochromated radiation (λ = 0.71073 Å) with a ϕ range of 0–200°, an increment of 1.0°, a 2θ range from 2.0–26°, and D_{max}–D_{min} = 12.45–0.81 Å. The structure was solved by direct methods using the program SHELXS-97.[24] The refinement and all further calculations were carried out by using SHELXL-97.[25] The hydrogen atoms were included in the calculated positions and treated as riding atoms by using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, by using a weighted full-matrix least-squares approach on F^2. Figure 5 was drawn with POV-Ray software.[26]

CCDC-295104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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