

Hydrogenation of Arenes over Catalysts that Combine a Metal Phase and a Grafted Metal Complex: Role of the Single-Site Catalyst**

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In comparison with the separate components, the combination on the same support material of dispersed palladium nanoparticles and grafted molecular rhodium complexes has provided evidence of improved activity in the hydrogenation of arenes.^[1] It was proposed that the catalytic efficiency is a consequence of a hydrogen-spillover process that would enhance specifically the hydrogenation activity of the molecular catalyst.^[1] A recent study of the hydrogenation of arenes with a catalyst obtained by silica sol-gel coentrapment of metallic palladium and $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ disagrees with the hydrogen-spillover hypothesis and suggests that the action of both metals is caused by a synergistic effect;^[2] however, no explanation of the nature of this effect has been forthcoming. Herein, we provide a rationale for this synergistic effect, and show that the grafted rhodium complex speeds up the hydrogenation of arenes to cyclic dienes.

Three different heterogeneous catalysts were tested in the hydrogenation of some arenes in *n*-pentane at relatively low temperature (40–60 °C) and 30 bar H_2 . A highly dispersed palladium metallic phase and the Rh^{I} complex $[\text{Rh}(\text{cod})(\text{sulphos})]$ (cod = cyclooctadiene; sulphos = $^-\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{-C}(\text{CH}_2\text{PPh}_2)_3$) were separately supported on high-surface-area porous silica. A calcination/reduction procedure of silica-supported PdCl_2 was employed to prepare Pd^0/SiO_2 , **1**, with a metal content of about 10 wt %, while the Rh^{I} complex was grafted by using a known procedure involving hydrogen bonds between silanols of the support and sulfonate groups from the sulphos ligand.^[3] The single-site catalyst, $[\text{Rh}(\text{cod})(\text{sulphos})]/\text{SiO}_2$, **2** (Figure 1 A) with a metal content of about 0.5 wt %, was previously employed to catalyze the hydrogenation and hydroformylation of olefins in either gas–solid or liquid–solid phase.^[3a] Upon hydrogenation, the cod ligand

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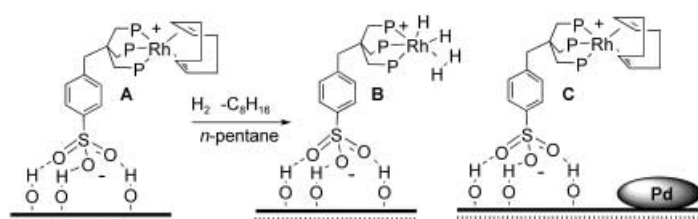


Figure 1. Sketches of the precursors employed in this study.

in **2** is removed as cyclooctane and replaced in the metal coordination sphere by hydride ligands.^[3a] Studies of model compounds showed that the most likely structure of Rh^{III} tetrahydride is nonclassical (Figure 1 B).^[4] The third catalyst, [Rh(cod)(sulphos)]–Pd⁰/SiO₂, **3**, was obtained by straightforwardly tethering the Rh^I precursor [Rh(cod)(sulphos)] onto **1** by using the same procedure adopted for **2** (Figure 1 C).^[3]

The high resolution transmission electron-microscopy (HRTEM) analysis of **1** showed a uniform particle dispersion with a narrow distribution centered at 1.65 nm, which is in good agreement with the value estimated from the EXAFS data. The surface area was found to decrease from 344 to 304 m² g^{−1} with a corresponding decrease in the pore volume from 1.19 to 1.02 cm³ g^{−1}. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and extended X-ray absorption fine-structure (EXAFS) measurements showed [Rh(cod)(sulphos)] to be tethered through hydrogen bonds on preformed **1** with no change in the chemical environment of the rhodium center. The surface area and pore volume for **3** were 284 m² g^{−1} and 0.95 cm³ g^{−1}, respectively. HRTEM data were consistent with a uniform palladium-particle dispersion with a mean size of 1.79 nm. Table 1 reports data obtained for the hydrogenation of benzene, toluene, styrene, and ethylbenzene. A unique sample of **3** containing a Pd/Rh molar ratio of 17.6:1 was used in all reactions. Irrespective of the arene, the combined single-site/dispersed-metal catalyst **3** was from four to six times more active than **1**, while **2** proved to be totally inactive. In contrast, the grafted Rh^I complex was as active as **1** for the hydrogenation of the styrene double bond (entries 7, 8).

Table 1: Hydrogenation of arenes with **1**, **2** or **3**.^[a]

| Entry | Catalyst | T [°C] | Substrate | Substrate/M ratio | % Conversion ^[b] (TOF, M) ^[c] product |
|-------|-------------------------|--------|--------------|-------------------|---|
| 1 | 1 | 40 | benzene | 525 | 4 (11) cyclohexane |
| 2 | 2 | 40 | benzene | 9200 | 0 |
| 3 | 3 | 40 | benzene | 525/9200 | 15 (39, Pd) cyclohexane |
| 4 | 1 ^[d] | 40 | toluene | 426 | 4 (8) methylcyclohexane |
| 5 | 2 ^[e] | 40 | toluene | 7520 | 0 |
| 6 | 3 ^[f] | 40 | toluene | 426/7520 | 16 (32, Pd) methylcyclohexane |
| 7 | 1 | 60 | styrene | 400 | 97 (194) ethylbenzene; 3 (6) ethylcyclohexane |
| 8 | 2 | 60 | styrene | 8750 | 98 (4287) ethylbenzene |
| 9 | 3 | 60 | styrene | 400/8750 | 81 (162, Pd) ethylbenzene; 19 (38 Pd) ethylcyclohexane |
| 10 | 1 | 60 | ethylbenzene | 400 | 3 (6) ethylcyclohexane |
| 11 | 2 | 60 | ethylbenzene | 8750 | 0 |
| 12 | 3 | 60 | ethylbenzene | 400/8750 | 20 (40, Pd) ethylcyclohexane |

[a] Experimental conditions: **1** (9.86 wt% Pd), 0.044 mmol Pd; **2** (0.56 wt% Rh), 0.0025 mmol Rh; **3** (0.56 wt% Rh, 9.86 wt% Pd), 0.044 mmol Pd, 0.0025 mmol Rh; 30 bar H₂; 30 mL *n*-pentane, 2 h, 1500 rpm. [b] Average values over at least three runs. [c] Mol product (mol M h)^{−1} (M = Pd, Rh). [d] 0.088 mmol Pd. [e] 0.005 mmol Rh. [f] 0.088 mmol Pd, 0.005 mmol Rh.

Catalyst **3** was also the best for the hydrogenation of cyclohexa-1,3-diene (Table 2). The presence of the grafted Rh^I complex apparently minimizes the amount of benzene produced by the dehydrogenation of cyclohexa-1,3-diene over the Pd particles (see entries 1 and 3).^[5] The ability of supported Pd⁰ particles to disproportionate cyclohexa-1,3-diene to benzene and cyclohexene is well-known, and the hydrogenation of benzene to cyclohexa-1,3-diene was proved to be the rate limiting step along the reduction to cyclohexane.^[5]

Table 2: Hydrogenation of cyclohexa-1,3-diene with **1**, **2** or **3**.^[a]

| Entry | Catalyst | Substrate/ M ratio | % Conversion ^[b] (TOF, M) ^[c] | | |
|-------|----------|-----------------------|---|-------------|-------------|
| | | | benzene | cyclohexene | cyclohexane |
| 1 | 1 | 525 | 27 (284) | 5 (52) | 68 (714) |
| 2 | 2 | 9200 | 0 | 11 (2024) | 2 (368) |
| 3 | 3 | 525/9200 | 6 (63, Pd) | 6 (63, Pd) | 88 (924 Pd) |

[a] Experimental conditions: **1** (9.86 wt% Pd), 0.044 mmol Pd; **2** (0.56 wt% Rh), 0.0025 mmol Rh; **3** (0.56 wt% Rh, 9.86 wt% Pd), 0.044 mmol Pd, 0.0025 mmol Rh; 30 bar H₂, 30 mL *n*-pentane, 25 °C, 30 min, 1500 rpm. [b] Average values over at least three runs. [c] Mol product (mol M h)^{−1} (M = Pd, Rh; TOF = turnover frequency).

Control experiments of the dehydrogenation of cyclohexa-1,3-diene under N₂ proved that **1** is an effective disproportionation catalyst (cyclohexane 2%, cyclohexene 46%, benzene 48% under the conditions of Table 2), while **2** is unable to perform such a reaction.

Finally, **1** proved much better than **2** for the hydrogenation of cyclohexene to cyclohexane (Table 3 entries 1, 3), and did not promote the dehydrogenation of cyclohexene as shown by a reaction under N₂ (Table 3, entry 2).

A number of independent experiments were performed to gain further insight into the role played by the tethered Rh^I catalyst in the hydrogenation of benzene. The hydrogenation was carried out in the presence of a mechanical mixture of **1** and **2** under the experimental conditions of Table 1, entry 3. No appreciable synergistic effect was observed, the conversion to cyclohexane being almost identical to that obtained with **1** alone.

Table 3: Hydrogenation of cyclohexene to cyclohexane with **1**, **2** or **3**.^[a]

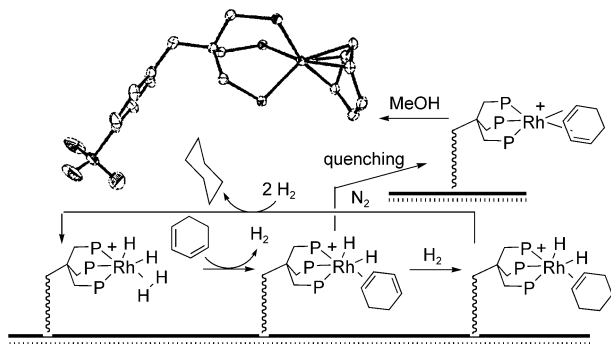
| Entry | Catalyst | Substrate/M ratio | % Conversion ^[b] (TOF, M) ^[c] |
|------------------|----------|-------------------|---|
| 1 | 1 | 525 | 99.8 (1048) |
| 2 ^[d] | 1 | 525 | 0 |
| 3 | 2 | 9200 | 0.5 (92) |
| 4 | 3 | 525/9200 | 100 (1050 Pd) |

[a] Experimental conditions: **1** (9.86 wt% Pd), 0.044 mmol Pd; **2** (0.56 wt% Rh), 0.0025 mmol Rh; **3** (0.56 wt% Rh, 9.86 wt% Pd), 0.044 mmol Pd, 0.0025 mmol Rh; 30 bar H₂; 30 mL *n*-pentane, 25 °C, 30 min, 1500 rpm. [b] Average values over at least three runs. [c] Mol product (mol Mh)⁻¹ (M = Pd, Rh). [d] Under 1 bar N₂.

The known Rh^I complex [Rh(CO)₂(sulphos)], unable to hydrogenate double bonds,^[3a] was anchored over **1**, and the resulting combined molecular–nanoparticle catalyst was used to hydrogenate benzene under the conditions of Table 1. The conversion to cyclohexane (4%) was similar to that observed in the presence of **1** alone (Table 1, entry 1).

Both **2** and the molecular precursor [Rh(cod)(sulphos)] did not hydrogenate arenes, irrespective of the phase variation, even at very high H₂ pressure, which rules out the promoting effect of an eventual hydrogen spillover promoted by palladium particles, and the action of leached Rh^I catalyst, respectively.

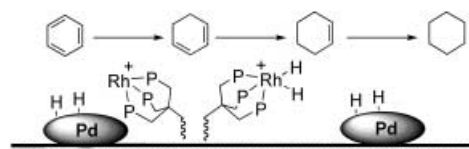
The hydrogenation of cyclohexa-1,3-diene in the presence of **2** under the conditions of Table 2, entry 2 was quenched after 30 min by depressurising the reactor, which was then replenished with N₂ (Figure 2). The solid compound was collected by filtration, dried in vacuo and treated with MeOD/[D₇]DMF (1:1, v/v) under N₂ to break the hydrogen bonds between the support and the molecular complex.^[3] ³¹P{¹H} and ¹H NMR spectra of the resulting solution showed the formation of [Rh(η⁴-C₆H₈)(sulphos)].^[6] Crystals of [Rh(η⁴-C₆H₈)(sulphos)]·2MeOH were obtained by reacting [Rh(cod)(sulphos)] with cyclohexa-1,3-diene in MeOH and authenticated by a single-crystal X-ray analysis.^[7] The structure consists of discrete molecules of [Rh(η⁴-C₆H₈)(sulphos)] with MeOH filling holes in the lattice (ORTEP drawing, Figure 2). Three *fac* phosphorus atoms and two double bonds from cyclohexa-1,3-diene coordinate the rhodium center in a distorted square-pyramidal geometry. The bond distances and angles are typical of metal complexes with either sulphos or MeC(CH₂PPh₂)₃ (triphos) and η⁴-dienes.^[3a,8]


Figure 2. Proposed mechanism for the formation of [Rh(η⁴-C₆H₈)(sulphos)].

The possibility that rhodium metal, eventually formed upon partial decomposition of the grafted complex, might contribute to enhance the hydrogenation activity of the palladium catalyst was ruled out on the basis of five recycling experiments that gave comparable conversions. Washing the recycled catalyst with MeOH to remove the grafted rhodium complex gave a much less active catalyst with a conversion to cyclohexane similar to that observed with **1** alone. Mechanistic details for cyclohexa-1,3-diene hydrogenation to cyclohexene were provided for [Ir(η⁴-C₆H₈)(triphos)]⁺.^[9]

The incorporation of the experimental evidence reported above leads us to conclude that 1) an intimate contact between the Pd nanoparticles and the Rh single sites in the mixed catalyst **3** is mandatory to observe improved activity in the hydrogenation of arenes to cycloalkanes; 2) the inhibition of diene disproportionation by the grafted rhodium complex, though important, cannot account alone for the increased conversions to cycloalkanes. These conversions are at least four times higher than those obtained with **1**, and even under the precondition that all cyclic dienes undergo disproportionation over palladium the total production of cycloalkane would not have been more than two times higher than that obtained with palladium alone. It is therefore reasonable to conclude that the grafted rhodium moieties cooperate with the palladium nanoparticles in promoting the hydrogenation of arenes to cyclic 1,3-dienes.

A simplified mechanism for the overall hydrogenation of benzene to cyclohexane is proposed in Figure 3, in which the rate-limiting hydrogenation of benzene to cyclohexa-1,3-diene is assisted by both palladium and rhodium centers. In view of the catalytic results reported in Table 2 and Table 3,


Figure 3. Proposed mechanism for the hydrogenation of benzene by **3**.

cyclohexa-1,3-diene should be more rapidly reduced to cyclohexene at rhodium, while cyclohexene should be predominantly reduced at palladium. The intimate mechanism of the Pd–Rh interaction in the first hydrogenation step is still rather obscure, yet its discovery is of paramount importance as it may open the door to the rational design of a new generation of tailored heterogeneous catalysts for diverse applications through appropriate combinations of supported metals and grafted molecular complexes.

Experimental Section

Details of the synthesis and characterization of the heterogeneous catalysts **1**, **2**, and **3** and of the complex [Rh(η⁴-C₆H₈)(sulphos)] are described in the Supporting Information.

Hydrogenation procedure: A stainless steel Parr reactor (100 mL), equipped with a temperature and pressure controller, and a paddle stirrer was charged with the appropriate amount of catalyst, the

unsaturated substrate, *n*-pentane (30 mL), and H₂ (30 bar). The ensemble was heated to the appropriate temperature and then stirred (1500 rpm) for the desired time, after which the vessel was cooled to ambient temperature and depressurised. The liquid contents were analysed by GC and GC-MS. Above 1500 rpm, the rates were independent of the agitation speed at all the temperatures studied, thus indicating the absence of mass transfer resistance.

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- [6] NMR Data ([D₇]DMF, 20 °C, *J* in Hz): ³¹P{¹H} NMR (81.01 MHz): δ = 11.0 ppm (d, ¹*J*(P,Rh) = 122.6); ¹H NMR (200.13 MHz): δ = 7.88 (d, ³*J*(H,H) = 8.1, 2H; *m*-H-SO₃C₆H₄), 7.71 (d, ³*J*(H,H) = 8.1, 2H; *o*-H-SO₃C₆H₄), 7.30 (m, 6H; *p*-H-PPh₂), 7.2–7.1 (m, 24H; *o*- and *m*-H-PPh₂), 6.61 (m, 2H; CH-C₆H₈), 3.52 (s, 2H; CH₂C), 3.45 (m, 2H; CH-C₆H₈), 2.91 (br s, 6H; CH₂P), 1.35 (m, 2H; Hβ(CH₂)-C₆H₈), 1.23 ppm (m, 2H; Hα(CH₂)-C₆H₈).
- [7] *Crystal data*: yellow crystals (0.3 × 0.25 × 0.25 mm), monoclinic, space group *P*2₁/*n*, *a* = 13.513(5), *b* = 18.308(5), *c* = 19.539(5) Å, β = 94.350(5)°, *V* = 4820(3) Å³, *Z* = 4, ρ_{calcd} = 1.415 g cm⁻³, μ = 0.546 mm⁻¹, Mo_{Kα} (λ = 0.71609 Å), *T* = 293(2) K, 6674 independent reflections. Refinement on all data converged at *R*₁ = 0.0678, *wR*₂ = 0.1113, GOF = 0.9912. CCDC-198527 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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