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Fullerene complexes with palladium and rhodium as catalysts for acetylenic bond hydrogenation

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The catalytic activity of the fullerene complexes (C_{60})Pd(PPh_3)$_2$, (C_{70})Pd(PPh_3)$_2$, (C_{60})Pd[(+)-DIOP] and (C_{60})RhH(CO)(PPh_3)$_2$ in the hydrogenation of acetylenic bond has been studied using diphenylacetylene as a model substrate.

Fullerenes are of interest because of their properties, such as hydrophobicity, electron-accepting ability, photoactivity and potential catalytic action (for metal complexes[1]). For example, a polymeric complex (C_{60})$_x$Pd$_y$, which is not an individual compound, is used as a catalyst in hydrogenation reactions and its catalytic properties can be explained by the presence of a metal palladium admixture.[2]

Previously[3,4] it was found that the pure palladium complex (η^2-C_{60})Pd(PPh_3)$_2$ catalyses the hydrogenation of acetylenic alcohols in solution. Here, we report that the complexes of fullerenes C_{60} and C_{70} with palladium and rhodium are catalytically active in the hydrogenation of the C≡C bond without functional groups.† The hydrogenation of diphenylacetylene **1** as a model substrate affords a mixture of *cis*-stilbene **2** and diphenylethane **3** (Scheme 1, Table 1).‡

As can be seen in Table 1, no Pd-catalysed tolan hydrogenation was observed in an aprotic solvent (benzene, entries 1, 3). The reaction proceeds only in a protic medium (C_6H_6/MeOH or C_6H_6/Pr^{i}OH, entries 2, 4–6). This effect is typical of homogeneous metal complex catalysis.[5] It is explained by the fact that the protic solvent facilitates H_2 heterolysis to give catalytically active metal hydride intermediates.[6] The addition of benzene to MeOH or Pr^{i}OH increases the solubility of fullerene complexes in these polar solvents. Tolane hydrogenation catalysed by complexes **I** and **II** under the same conditions (C_6H_6/MeOH, 60 °C) gave similar results with both catalysts (*cf.* entries 2 and 6). These conditions are likely to be optimal as an increase in the reaction temperature up to 100 °C causes catalyst deactivation (entry 4). Rhodium complex **IV** showed the highest catalytic activity: 75% conversion at 60 °C (entry 10).

1 **2** **3**

Catalysts:
I (C_{60})Pd(PPh_3)$_2$
II (C_{70})Pd(PPh_3)$_2$
III (C_{60})Pd[(+)-DIOP]
IV (C_{60})RhH(CO)(PPh_3)$_2$

Scheme 1

Table 1 Hydrogenation of diphenylacetylene **1** catalysed by fullerene complexes **I**–**IV**.[a]

Entry	Catalyst	Reaction conditions: Solvent[b]	Reaction conditions: *T*/°C	Conversion (mol%)	TON[c]/ h^{-1}	Reaction products (mol%): 2	Reaction products (mol%): 3
1	**I**	C_6H_6	50	Traces	—		
2	**I**	C_6H_6/MeOH	60	35	5.5	60	40
3	**II**	C_6H_6	50	—	—	—	—
4	**II**	C_6H_6/Pr^{i}OH	100	9	1.4	80	20
5	**II**	C_6H_6/Pr^{i}OH	80	21	3.3	83	17
6	**II**	C_6H_6/MeOH	60	36	5.6	67	33
7	**III**	C_6H_6/Pr^{i}OH	80	38	5.9	76	24
8	**IV**	C_6H_6/Pr^{i}OH	80	63	9.8	58	42
9	**IV**	C_6H_6/MeOH	80	73	11.4	21	79
10	**IV**	C_6H_6/MeOH	60	75	11.7	58	42

[a] [Substrate]/[catalyst] = 120–130, [**1**] = 0.23 mol dm^{-3}, *P* = 20 atm (H_2), 8 h. [b] C_6H_6/alcohol = 1:1 (v/v). [c] Turnover number.

In contrast to the reduction of an acetylenic bond in the presence of palladium complexes, they did not catalyse the hydrogenation of the carbonyl group (acetophenone was used as a starting reagent). In the case of rhodium complex **IV** as a catalyst, 8% acetophenone conversion could be achieved (C_6H_6/Pr^{i}OH = 1:1, 40 atm H_2, 80 °C, 9 h).

Thus, the Pd^0 and Rh^I fullerene complexes show catalytic activity in the hydrogenation of the C≡C bond, but they are inactive or weakly active in the hydrogenation of the C=O bond.

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† Fullerene metal complexes were obtained according to published procedures[7–9] and recrystallised from toluene. They were characterised by elemental analysis data and ^{1}H and ^{31}P NMR spectra. The complexes were kept and handled under an argon atmosphere. Argon was purified by passing through columns containing a nickel–chromium catalyst, copper supported on Kieselguhr (80 °C) and molecular sieves. Hydrogen was purified by passing through columns with a nickel–chromium catalyst and molecular sieves. Hydrogenation products were analysed by ^{1}H NMR spectroscopy on a Bruker AM-300 instrument.

‡ A catalyst (3.6 μmol) and tolan (0.45 mmol) were placed in a glass tube for hydrogenation, the tube was three times evacuated and filled with argon. A degassed solvent (2 ml) was added to the tube, and the latter was placed in a stainless steel autoclave (50 ml) filled with argon. The autoclave was purged with hydrogen, and the H_2 pressure was adjusted to 20 atm. The reaction mixture was magnetically stirred (700 rpm) in the course of hydrogenation.

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