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Preliminary communication

TOLUENE-SOLVATED RHODIUM ATOMS: EVIDENCE FOR A HYDRIDORHODIUM COMPLEX

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Summary

The codeposition of rhodium with toluene affords on melting a red brown solution, stable up to −50°C, which contains a hydridorhodium product, as shown by ^{1}H NMR analysis and isolation of hydrido complexes by reaction with phosphines.

Co-condensation of transition metal atoms with arenes is an established way of preparing bis-arene-metal derivatives [1]. However, the co-deposition products are often stable only at low temperature in the arene solution, and no definite compounds can be isolated. Such weakly stabilized species have recently proved to be valuable precursors for organometallic synthesis and preparation of catalysts [2,3]. Very little is known on the nature of these so called arene "solvated" metal atoms; they are assumed to be very labile zerovalent π-arene complexes with a relatively strongly bonded η^6-π-arene and a weaker η^4- or η^2-π-arene bond [2].

In order to gain a better inside into the structure of such solvated metal atoms we studied the reaction of Rh atoms and toluene and we present here evidence for the presence of a hydridorhodium complex as co-deposition product.

Rhodium vapour, obtained by resistive heating of tungsten wire surface-coated with electrodeposited rhodium, reacts at −196°C with toluene to give a red brown matrix which does not deposit metal on melting. The co-deposition product can be taken up into toluene at −70°C and the solution handled at temperatures up to −50°C. At higher temperatures it decomposes, partially depositing the rhodium as metal.

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The possibility that the co-deposition product is a zerovalent metal complex can reasonably be ruled out on the basis of the following observations. The reaction solution does not give an ESR signal in the temperature range −50°C to −100°C. The ^{1}H NMR spectrum at −70°C shows a hydrido signal at δ −13.5 ppm; this signal appears as a well resolved quartet, with J(Rh—H) 8 Hz (Fig. 1). Such a multiplicity, which could originate, as observed in other hydridorhodium complexes [4], from magnetically equivalent hydrogen atoms spin-coupled equivalently with three Rh atoms, indicates the presence of a trinuclear hydridorhodium cluster. The hydrido signal disappears on warming to temperatures higher than −50°C, at which the sample decomposes.

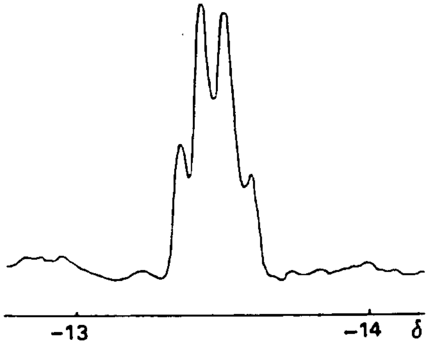
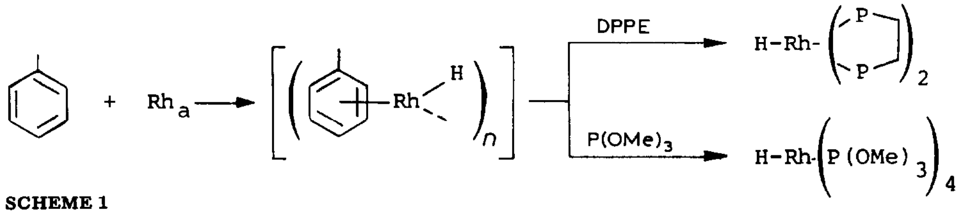


Fig. 1. The hydridic (Rh—H) portion of the 100 MHz ^{1}H NMR spectrum of the co-condensation product, in toluene solution at —70° C.

The presence of the hydrido structure is supported by the observation that treatment with excess trimethylphosphite (TMP) or 1,2-bis(diphenylphosphino)ethane (DPPE) gives the known HRh(TMP)$_4$ and HRh(DPPE)$_2$ derivatives (Scheme 1), which have been characterized by elemental analysis and comparison of their IR and ^{1}H NMR spectra with those of authentic samples [4,5].



SCHEME 1

When perdeuterotoluene was used in the preparation of the co-deposition product, DRh(DPPE)$_2$ was obtained after addition of 1,2-bis(diphenylphosphino)ethane, showing toluene to be the hydrogen source for the hydrido complex. The presence in the reaction solution of dibenzyl, identified by GLC and mass spectrometry, provides further evidence that the toluene is the hydrogen source, and that there is a sp^3 C—H bond activation.

A possible mechanism for the formation of a hydridorhodium complex by co-deposition of Rh atoms and toluene could involve oxidative addition of toluene to rhodium(0) species to form an alkylrhodium(II) hydride, followed by homolysis of the rhodium—alkyl bond. Such carbon—hydrogen bond activation has been often observed in metal atom chemistry, and can also provide a new type of route to hydrido-transition metal complexes [6].

Studies in progress show that this hydridorhodium-toluene co-deposition product is extremely reactive, and a very promising catalyst for a wide range of reactions, such as the hydrogenation of carbocyclic and heterocyclic aromatic compounds [7], the selective hydroformylation of dienes to alkenecarboxyaldehydes [8], and the synthesis of pyridines from acetylenes and nitriles [8].

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