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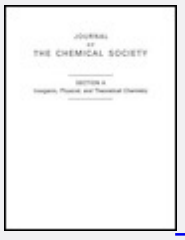

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The preparation and properties of tris(triphenylphosp some reactions thereof including catalytic homogeneo acetylenes and their derivatives

J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson

Abstract

Tris(triphenylphosphine)chlororhodium(I), $RhCl(PPh_3)_3$, has been prepared by the with rhodium(III) chloride hydrate in ethanol; the corresponding bromide and iodi complex in various solvents has been investigated, and its reactions with hydrogen, studied. Dihydrido- and ethylene complexes have been isolated and studied by nuc Approximate values for the formation constants of ethylene and propylene complex factor of over 10^3. By electron spin resonance spectroscopy, the complex $RhCl(PPh_3)$ paramagnetic species, probably a rhodium(II) complex.

In homogeneous solution the tris(triphenylphosphine) complexes are exceedingly a hydrogenation, at *ca.* 1 atmosphere of hydrogen pressure and room temperature, of olefinic and acetylenic linkages.

The rates of hydrogenation of hept-1-ene, cyclohexene and hex-1-yne have been stu factors such as substrate and catalyst concentration, temperature, and pressure det rate expression of the form: Rate $=K_p[S][A]//_{1+K_{1p}+K_2[S]}$ where [S] and [A] are the olefin is the concentration of hydrogen in solution.

From the data for cyclohexene the activation energy for the rate determining step is mole^{-1}) and the value of Î”*S*â ¡= 12Â·9 e.u.

It is shown that the rate of hydrogenâ “deuterium exchange under selected conditi hydrogenation of olefins and, furthermore, that when H_2â “D_2 mixtures are used in the major products. Reductions of maleic and fumaric acids with deuterium shows in the reduction of hex-2-yne to n-hexane, *cis*-hex-2-ene is found to be the major ol

A mechanism for the hydrogenation is proposed in which the metal complex serves and an olefin molecule are briefly co-ordinated before transfer of one to the other ta H_2/rate D_2= 0Â·9) suggests that synchronous breaking of Rhâ “H bonds and making state involving two simultaneous three-centre interactions.

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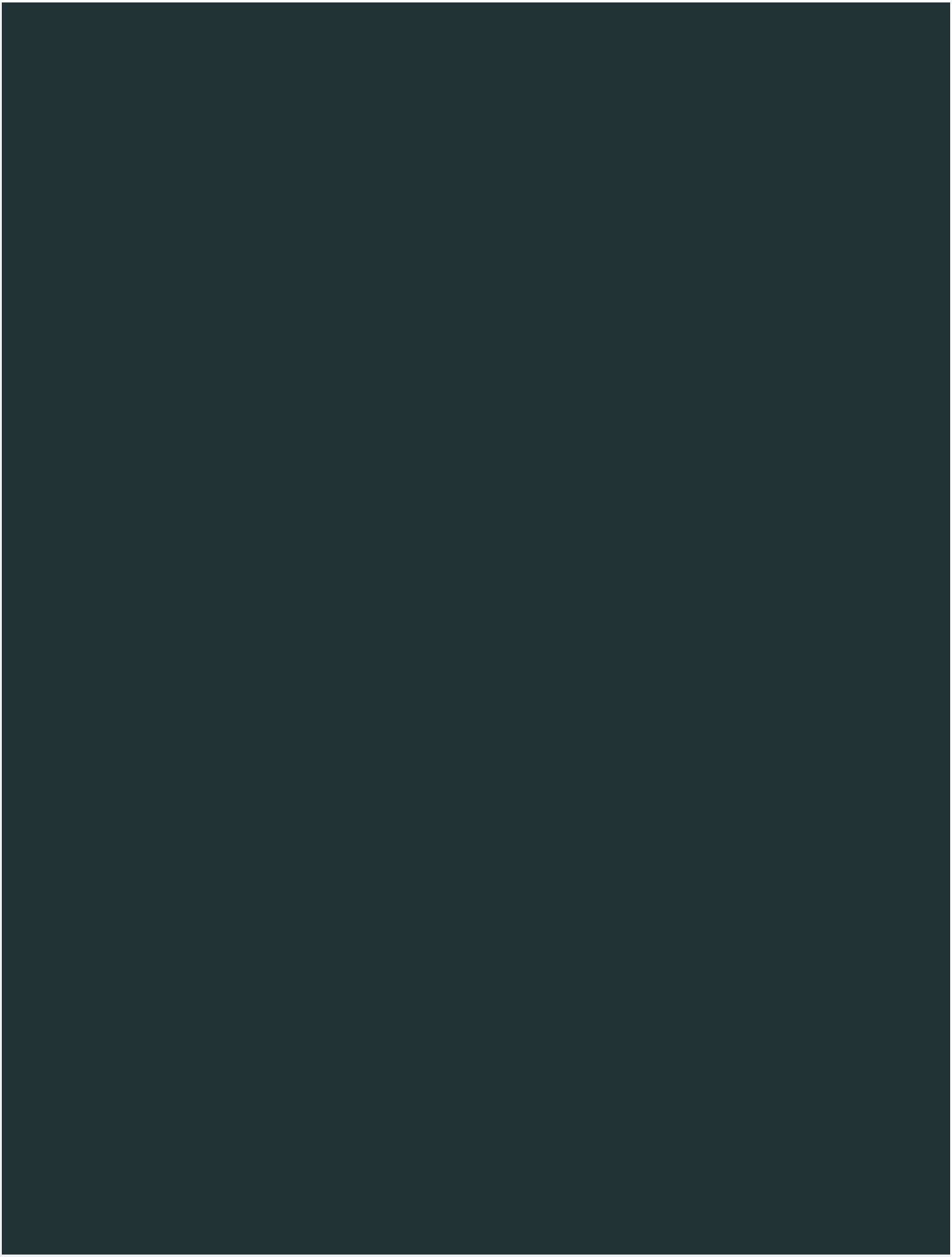

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