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Reaction of $(PPh_3)_2ReH_7$ with Dienes: Preparation and Some Properties of Trihydrido η^4-Diene and Dihydro η^5-Dienyl Complexes of Rhenium

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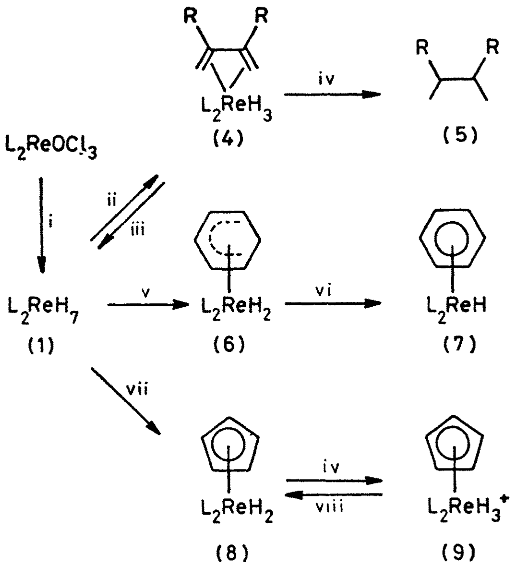
Summary The title compound reacts with dienes to give trihydrido η^4-diene or dihydrido η^5-dienyl complexes; pyrolysis of the η^5-cyclohexadienyl compound (**6**) gives the hydrido arene complex (**7**), and protonation of the η^4-diene compounds (**4**) leads to complete hydrogenation of the dienes.

The rhenium heptahydride (**1**)[1] readily reacts with ligands L′ (tertiary phosphines, arsines, and amines) to afford the pentahydrides (**2**);[1] the latter are much less reactive, and vigorous conditions are required to obtain the trihydrides

$$\underset{(\mathbf{1})}{(PPh_3)_2ReH_7} \xrightarrow{L'} \underset{(\mathbf{2})}{(PPh_3)_2L'ReH_5} \xrightarrow{L'} \underset{(\mathbf{3})}{(PPh_3)_2L'_2ReH_3}$$

(**3**).[2] Here we report that the reaction of the heptahydride (**1**) with dienes leads directly, under mild conditions [refluxing for 15 min in tetrahydrofuran (THF) with a ten fold excess of diene†] to rhenium trihydrido η^4-diene and dihydrido η^5-dienyl complexes (Scheme); these undergo some interesting reactions and constitute a new entry into organorhenium chemistry.

The pale yellow diene complexes (**4**) [τ(CD_2Cl_2): R = H: 6·5, 8·1, and 11·5 (2H + 2H + 2H, br, η^4-C_4H_6) and 16·1 (3H, br t, *J* 25 Hz, ReH_3); R = Me: 8·3 and 11·6 (2H +



Scheme. (L = PPh_3; R = H and Me) i, $LiAlH_4$‡, ii, CH_2=CR–CR=CH_2, iii, H_2, 50 °C, 50 atm (R = Me), iv, HPF_6 in CH_2Cl_2, v, 1,3- or 1,4-cyclohexadiene, vi, 150 °C, 0·3 mmHg, 5 min, vii, cyclopentene or cyclopentadiene, viii, 1,4-diazabicyclo[2.2.2]octane.

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† Butadiene was bubbled through a refluxing solution of (**1**) in THF.

‡ The procedure described in ref. 1 was slightly modified. A suspension of $(PPh_3)_2ReOCl_3$ (1 mmol) in dry diethyl ether (50 ml) was stirred at room temperature with $LiAlH_4$ (3 mmol) for 30 min; the mixture was filtered, the solvent evaporated, and the residue extracted with wet dichloromethane; (**1**) was isolated in 60% yield.

2H, br, η^4-C_6H_{10}), 8·45 (6H, s, 2 Me), and 16·6 (3H, br t, *J* 29 Hz, ReH_3)] were formed from butadiene (70%) and 2,3-dimethylbuta-1,3-diene (65%), respectively. Protonation of the trihydrido complexes (**4**) at room temperature led to the production of the saturated hydrocarbons [**5**; R = H and Me (70% by g.l.c.)]. When the protonation was carried out with an excess of HCl, $(PPh_3)_2ReCl_4$[3] was formed (35%). Hydrogenation of (**4**; R = Me) led to a mixture of (**5**; R = Me) and 2,3-dimethylbut-1-ene, and regenerated the heptahydride (**1**).

The reaction of (**1**) with either 1,3- or 1,4-cyclohexadiene gave the dihydrido cyclohexadienyl compound (**6**) (70%) [τ(C_5D_5N): 6·6, 8·4, and 9·3 (7H, br, η^5-C_6H_7), 15·8 (2H, br t, *J* 28 Hz, ReH_2)]. Similarly, cyclopentadiene gave the dihydridocyclopentadienyl compound (**8**) (60%) [τ (CD_2Cl_2): 5·85 (5H, s, η^5-C_5H_5) and 25·5 (2H, t, *J* 40 Hz, ReH_2]. Compound (**8**) was also obtained (20%) by treatment of (**1**) with cyclopentene. Compounds (**6**) and (**8**) are colourless, air-stable, crystalline compounds; their mass spectra exhibit a signal at $M - 2$ corresponding to the loss of one molecule of hydrogen. Compound (**8**) could be reversibly protonated to (**9**) [τ (CD_2Cl_2): 5·4 (5H, s, η^5-C_5H_5) and 16·3 (3H, br t, *J* 30 Hz, ReH_3)]. Dehydrogenation of (**6**), by heating *in vacuo*, gave the yellow benzene derivative (**7**) [τ (C_6D_6): 5·9 (6H, s, η^6-C_6H_6) and 17·2 (1H, t, *J* 36 Hz, ReH)], in 20—50% yield.

The mild conditions under which the diene and dienyl compounds (**4**), (**6**), and (**8**) are formed are in striking contrast to the vigorous conditions required to obtain the trihydrides (**3′**; L′ = *e.g.* tertiary phosphine). Presumably the heptahydride (**1**) easily eliminates one mole of dihydrogen to afford the corresponding pentahydride [which then reacts with a mole of ligand L′ to give (**2**)], but the spontaneous elimination of dihydrogen from (**2**; L′ = *e.g.* tertiary phosphine) is much more difficult. In the reaction with dienes, the olefin ligand in the intermediate (**2**; L′ = η^2-diene) clearly assists the reaction by acting as a hydrogen acceptor; thus, when (**4**; R = Me) is prepared from (**1**) and an excess of 2,3-dimethylbuta-1,3-diene, one mole of hydrogen ends up as 2,3-dimethylbut-1-ene (70%) and alkane (**5**; R = Me) (15%).

All the new compounds [except (**9**), which was not isolated] gave satisfactory elemental analyses.

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