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Preliminary communication

FORMATION OF $(PPh_3)_2(\eta^5$-CYCLOHEXADIENYL)ReH_2 FROM THE REACTION OF $(PPh_3)_2ReH_7$ WITH BENZENE AND 3,3-DIMETHYLBUTENE

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Summary

L_2ReH_7 ($L = PPh_3$) reacts with 3,3-dimethylbutene and benzene (the latter being used as solvent) to give the dihydridocyclohexadienyl compound $L_2(\eta^5\text{-}C_6H_7)ReH_2$, the X-ray crystal structure of which is reported. With deuteriobenzene, the reaction gives a product which is partially deuteriated at the rhenium atom and in the *ortho*-positions of the phosphine ligands.

η^5-Cyclohexadienyl-transition metal complexes are generally prepared either by protonation of η^6-arene compounds or by hydride abstraction from η^4-cyclohexadiene derivatives [1]. We report below the synthesis of the η^5-cyclohexadienyl complex (VIII) from the reaction of $(PPh_3)_2ReH_7$ (I) with 3,3-dimethylbutene (II) in benzene.

The heptahydride (I) [2] and 3,3-dimethylbutene (II) (5 eq.) were refluxed in benzene for 10 minutes; the dihydrido cyclohexadienyl complex (VIII) was recrystallised from acetone and isolated in 70% yield as air-stable yellow crystals*. One mol of dihydrogen was evolved and 1.1 mol of 2,2-dimethylbutane (III) (GLC) was formed during the reaction.

The ^1H NMR spectrum of VIII shows the characteristic pattern [3] of the cyclohexadienyl ligand [$\tau(CD_2Cl_2)$: 3.65 (1 H, t, J 5 Hz), 6.55 (2 H, t, J 5 Hz),

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*The structure of VIII was previously erroneously assigned [4] to the compound obtained from the reaction between I and 1,3- or 1,4-cyclohexadiene. This compound is, in fact, $(PPh_3)_2(\eta^4$-1,3-cyclohexadiene)ReH_3 [$\tau(CD_2Cl_2)$, −50°C: 13.15 (1 H, t, J 38 Hz), and 18.05 (2 H, t, J 19 Hz)] (D. Baudry, M. Ephritikhine and H. Felkin, submitted to J. Organometal. Chem.).

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6.60 (1 H, m), 7.65 (1 H, m), and 8.05 (2 H, t, *J* 5 Hz)]; because of coalescence, the hydride signals are not visible in the spectrum at 34°C but at −40°C give rise to two triplets, each of intensity 1 (τ(CD_2Cl_2): 13.1 (*J* 36 Hz) and 22.7 (*J* 38 Hz)).

Dehydrogenation of VIII by heating in vacuo gives the arene derivative IX [4].

Crystals of VIII suitable for X-ray structural analysis were obtained from acetone, and the structure of VIII is shown in Fig. 1*. The two hydride ligands were not detected in the difference map; they presumably occupy two inequivalent *trans* positions in the C(1)—C(4)—Re plane. The latter is orthogonal to the P(1)—P(2)—Re plane.

The reaction between I, II, and deuteriobenzene gave partially deuteriated VIII. The NMR spectra of this compound in CD_2Cl_2 at −50°C and in C_6D_6 (in which the signals of the *ortho*-hydrogens in the phosphine ligands are separated from those of the *meta*- and *para*-hydrogens) indicated that it contained ca. 50 atom-% D in all positions of the cyclohexadienyl ring, ca. 25 atom-% D on the metal, and 10–15 atom-% D in the *ortho*-positions of the phosphine ligands. The dihydrogen evolved contained less than 5% HD (mass spectral analysis).

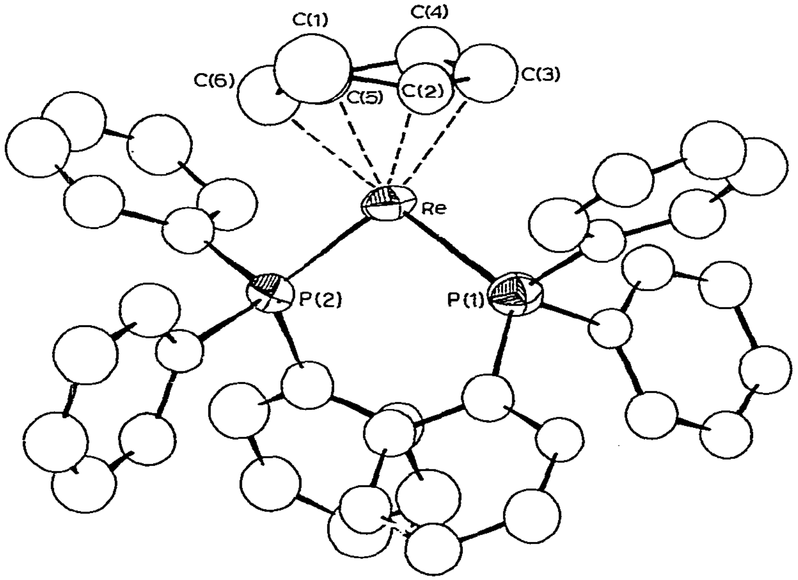

Fig. 1. ORTEP representation of $(PPh_3)_2(\eta^5\text{-}C_6H_7)ReH_2$ (VIII). The two hydride ligands were not detected in the difference map. Important mean bond lengths (Å) and angles (°) are: Re—P 2.355(5); Re—C(1) 2.72(5); Re—C(2) 2.26(3); Re—C(3) 2.28(4); Re—C(4) 2.38(4); Re—C(5) 2.23(3); Re—C(6) 2.25(4); P(1)—Re—P(2) 105.6(2).

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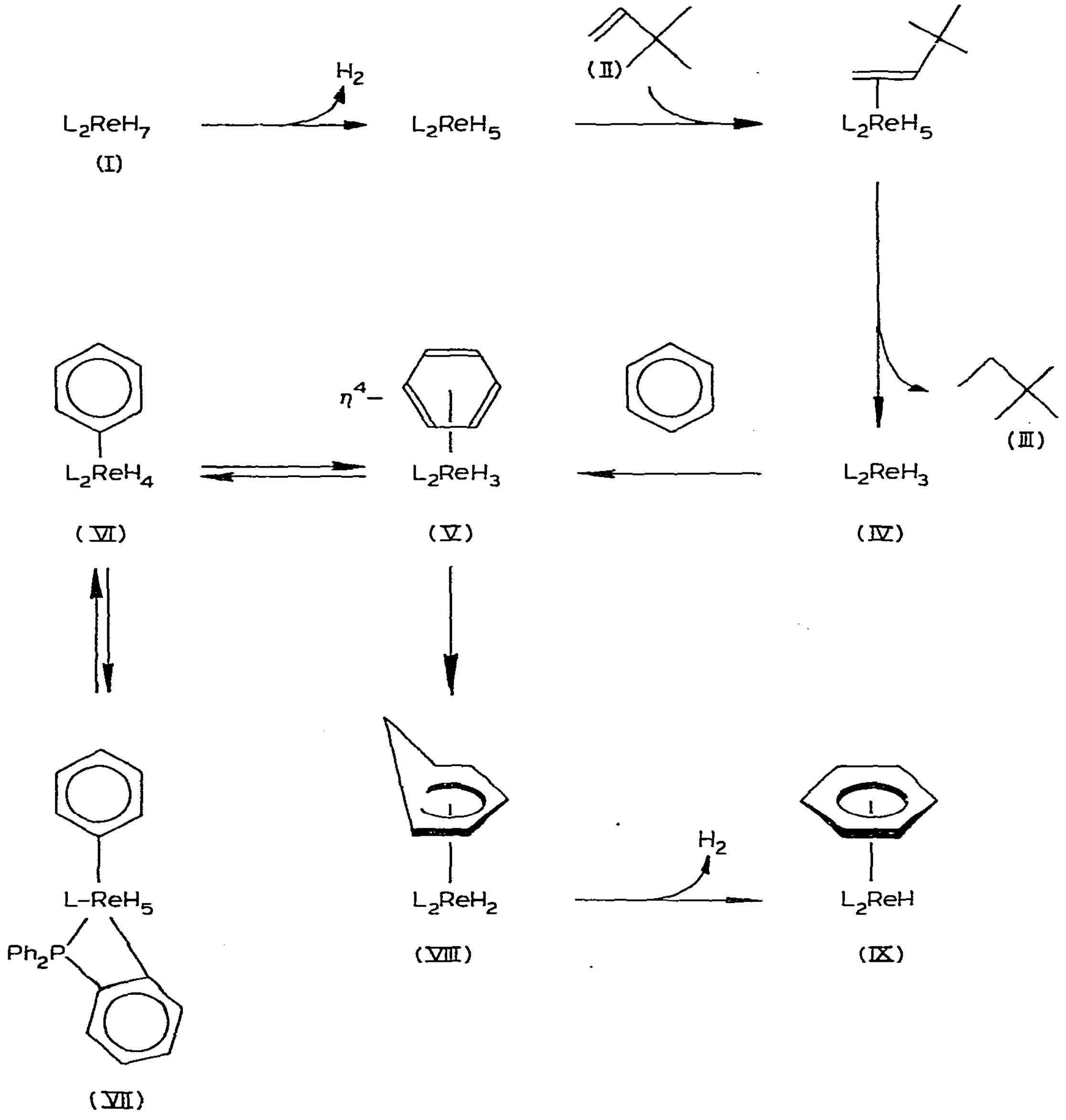
*Crystal data for VIII: $C_{42}H_{39}P_2Re$. monoclinic, space group $P2_1/n$, *a* 25.457(3), *b* 14.812(2), *c* 9.955(1) Å, *U* 3753 Å, β 90.50°, $Z = 4$, D_c 1.40 g cm^{-3}, $I/\sigma(I) > 2$, μ 8.8 cm^{-1}, θ-range 1.5—25°. Current *R*-value 0.082 for 4761 reflections (Mo-K_α radiation) and further refinement is in progress. The atomic coordinates are available from the authors on request.

These facts can be accounted for by the reaction sequence shown in Scheme 1, in which the 14*e* trihydrido intermediate IV (which we also assume to be responsible for the "activation" of cyclopentane) [5] combines rapidly and irreversibly with benzene to form the η^4-arene complex (V); intramolecular hydrogen transfer then leads irreversibly to the η^5-cyclohexadienyl dihydride VIII. Presumably the η^4-arene intermediate V is sufficiently long-lived to equilibrate partially with the phenyl tetrahydride VI, leading to exchange of protons between the metal and the ring, and also, via VI, with the



SCHEME 1. (L = PPh_3)

ortho-metallated species VII, resulting in exchange of protons between the metal and the phosphine ligands.

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