Interaction of Buta-1,3-diene with Co-ordinatively Unsaturated Binuclear Rhodium Hydrides; Synthesis and *X*-Ray Crystal Structure of [Rh$_2$(Pr$^i_2$PCH$_2$CH$_2$PPr$^i_2$)$_2$(μ-H)(μ-η^4-σ-C$_4$H$_5$)]

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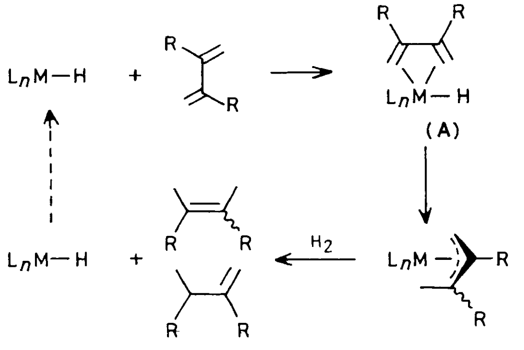
Reaction of buta-1,3-diene with [Rh$_2$(Pr$^i_2$PCH$_2$CH$_2$PPr$^i_2$)$_2$(μ-H)$_2$] leads to [Rh$_2$(Pr$^i_2$PCH$_2$CH$_2$PPr$^i_2$)$_2$(μ-H)(μ-η^4-σ-C$_4$H$_5$)], while the analogous reaction with [Rh$_2$\{(Pr^{i}O)$_2$PCH$_2$CH$_2$P(OPr^i)$_2$\}$_2$(μ-H)$_2$] initially generates a mixture of the but-1-enyl-hydride dimers, [Rh$_2$\{(Pr^{i}O)$_2$PCH$_2$CH$_2$P(OPr^i)$_2$\}$_2$(μ-H)(μ-η^2-C$_4$H$_7$)], that subsequently decomposes to a *syn–anti* mixture of [Rh(η^3-1-MeC$_3$H$_4$)\{(Pr^{i}O)$_2$PCH$_2$CH$_2$P(OPr^i)$_2$\}] in the presence of excess of butadiene.

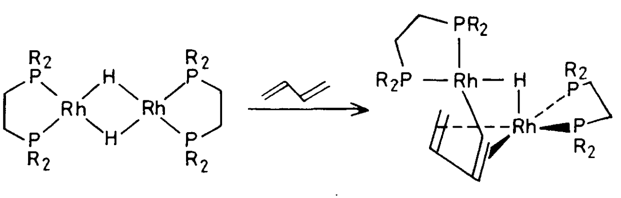
The reaction of 1,3-dienes with mononuclear transition metal hydrides is a versatile synthetic method for the production of substituted allyl complexes;[1] the intermediacy of mononuclear allyl derivatives by this route has also been invoked[2] in the selective hydrogenation of 1,3-dienes to monoenes (Scheme 1). The presumed diene–hydride precursor (**A**) has been isolated and structurally characterized only in rare instances[3] where either steric constraints[4] or electronic effects[5] disfavour the hydride-transfer step.



Scheme 1

With polynuclear metal hydrides, the reaction of 1,3-dienes is more complicated and simple allyl derivatives are usually not observed.[6] For example, the reaction[7] of buta-1,3-diene with the triosmium cluster Os$_3$H$_2$(CO)$_{10}$ leads to a mixture of Os$_3$(CO)$_{10}$(η^4-s-*cis*-C$_4$H$_6$) and Os$_3$(CO)$_{10}$(μ-η^2-η^2-s-*trans*-C$_4$H$_6$). Polynuclear metal carbonyls react with 1,3-dienes to generate complex product mixtures[8,9] which appear to involve C–H activation and/or C–C bond formation.

In an effort to understand how catalytically active polynuclear metal hydrides differ from their mononuclear counter-



(1)

(1) R = Pr^i (3)

parts, we have been investigating the reactions of hydrocarbon substrate molecules with co-ordinatively unsaturated rhodium hydride clusters.[10,11] We report here the reaction of buta-1,3-diene with the binuclear complexes $[Rh_2(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2(\mu\text{-}H)_2]$ (**1**)[10] and $[Rh_2\{(Pr^iO)_2PCH_2CH_2P(OPr^i)_2\}_2(\mu\text{-}H)_2]$ (**2**)[11] wherein we have observed: (i) a new type of bridging mode for the buta-1,3-dienyl ligand, and (ii) the remarkable influence of the phosphorus donor substituents on the course of the reaction.

The reaction of buta-1,3-diene ($\geqslant$2 equiv.) with (**1**) proceeds rapidly (<5 min) even at −10 °C as evidenced by a fast colour change from dark green to bright orange; yellow-orange crystals of the formula $[Rh_2(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2]\cdot C_4H_6$ (**3**) can be isolated in >90% yield (equation 1). The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of (**3**) are complex and temperature-dependent, to the extent that unambiguous structure analysis by 'sporting' methods was not possible. Fortunately, we were able to obtain single crystals suitable for *X*-ray diffraction; the preliminary results are shown in Figure 1 along with a number of pertinent bond parameters.

Crystal Data:† (**3**), $C_{32}H_{70}P_4Rh_2$, $M = 784.62$, triclinic, space group $P\bar{1}$, $a = 12.505(1)$, $b = 17.627(1)$, $c = 17.865(3)$ Å; $\alpha = 96.71(1)$, $\beta = 90.44(1)$, $\gamma = 101.14(6)°$; $Z = 4$ (2 molecules per asymmetric unit), $U = 3835.31$ Å^3, $D_c = 1.361$ g cm^{-3}; μ (Mo-K_α) = 10.31 cm^{-1}; present R factor = 0.039 for 7029 reflections with $I/\sigma(I) \geqslant 3.0$ collected on a Nonius CAD-4 diffractometer in the 2θ range 3—45°.

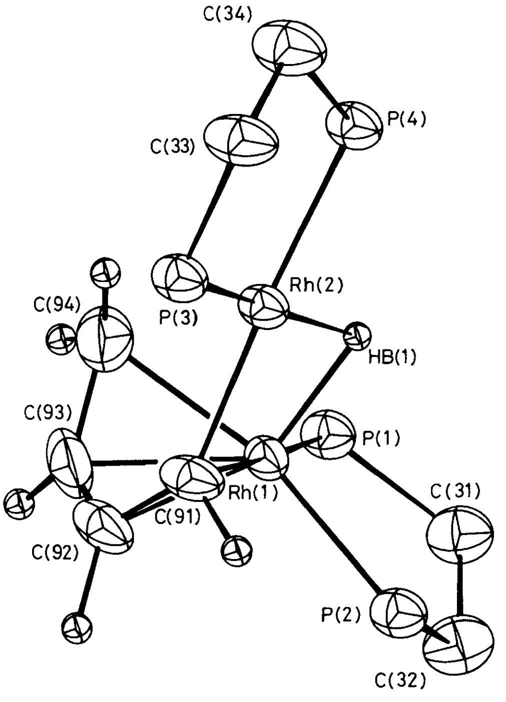
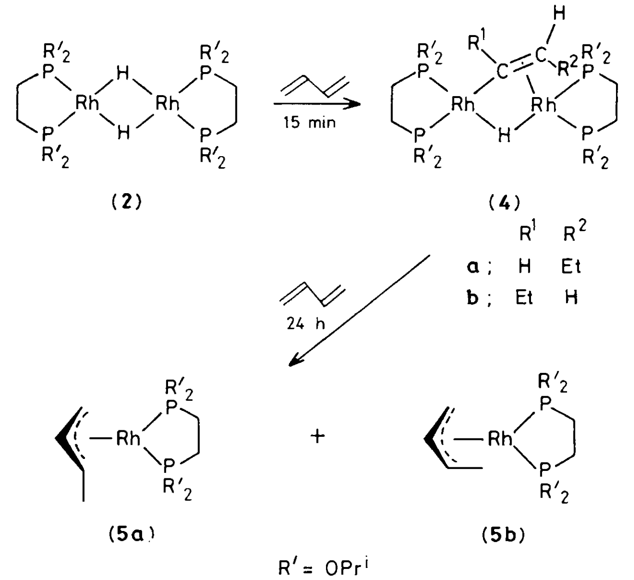


Figure 1. A view of (**3**) depicting the co-ordination environments around each rhodium centre (SNOOPI diagram; 50% probability contours for all atoms; isopropyl groups have been omitted for clarity). Selected bond parameters, Å: Rh(1)–Rh(2), 2.8105(8); Rh(1)–C(91), 2.219(7); Rh(1)–C(92), 2.272(7); Rh(1)–C(93), 2.181(8); Rh(1)–C(94), 2.231(8); Rh(2)–C(91), 2.053(8); Rh(1)–H_B, 1.8184(2), Rh(2)–H_B, 1.8742(2); C(91)–C(92), 1.428(11); C(92)–C(93), 1.400(13); C(93)–C(94), 1.427(14).

The butadienyl unit bridges the two rhodium centres *via* an η^4-*cis* attachment to Rh(1) and a σ bond from C(91) to Rh(2). The geometry around Rh(1) can be described as square-pyramidal with the hydride ligand occupying the apical site; we believe that the temperature-dependent ^1H and $^{31}P\{^1H\}$ n.m.r. spectra are due, in part, to intramolecular rearrangements[12] of the five-co-ordinate geometry about Rh(1). The geometry at Rh(2) is nearly square-planar.

To our knowledge, a 1,3-diene–hydride complex of rhodium(I) has not previously been isolated or observed;[13,14] undoubtedly, the hydride transfer step to generate the corresponding allyl derivative from (**3**) is disfavoured because of the unusual bonding mode of the butadienyl unit and the bridging nature of the hydride ligand. Attempts to induce hydride transfer in (**3**) by heating have only lead to decomposition.

The corresponding reaction of buta-1,3-diene with the isopropoxy derivative (**2**) takes a completely different course. The initial products (after ~15 min at 25 °C with excess of buta-1,3-diene) are a ~4 : 1 mixture of the but-1-enyl-hydride dimers (**4a**) and (**4b**) respectively (Scheme 2); this isomeric mixture reacts further (over a period of hours at 25 °C) with the excess of buta-1,3-diene to generate the mononuclear 1-methylallyl complexes (**5a**) and (**5b**) (~1 : 1). In the absence of excess of buta-1,3-diene, the formation of (**5a**) and (**5b**) is suppressed. The but-1-enyl-hydride isomers (**4a**) and (**4b**) were characterized by analogy with other work[10] from our laboratory, while the spectroscopic‡ data for the 1-methylallyl



Scheme 2

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ N.m.r. data: (**4a**), ^1H, $\delta(C_6D_6)$ 8.71 (br. d, J 10 Hz, RhCH=CH), 7.26 (sept., J_{PH} 5 Hz, RhCH=CH), and 2.65 (br. s, CH_2Me); CH$_2$$Me$ obscured. (**4b**), ^1H, $\delta(C_6D_6)$ 6.54 (m, RhCEt=CH); RhCEt=CH and Et obscured; ligand 4.99 (m, POCHMe$_2$), *ca.* 2.0 (m, PCH_2CH_2P), and *ca.* 1.5 (overlapping d, POCHMe_2). (**5a**), ^1H, $\delta(C_6D_6)$ (see Table III in ref. 15 for allyl proton labelling) 4.97 (m, H^1), 3.74 (m, $J_{1,2}$ 7.3 Hz, H^2), 3.37 (sext., $J_{1,4}$ 6.0, J_{Me} 5.5 Hz, H^4), 2.30 (q, J_{PH} 5.5 Hz, Me), and 2.07 (dd, $J_{1,3}$ 13.2, J_{PH} 6.0 Hz, H^3); $^{31}P\{^1H\}$ [C_7D_8, p.p.m. relative to $P(OMe)_3$ at +141.0 p.p.m.], AMX (X = ^{103}Rh): P^A 210.2 (dd, $^1J_{RhP}$ 261, $^2J_{AM}$ 4.9 Hz); P^M 199.3 (dd, $^1J_{RhP}$ 262 Hz). (**5b**), ^1H, $\delta(C_6D_6)$ 4.83 (m, H^5), 3.85 (m, $J_{5,6}$ 8.0 Hz, H^6), 2.39 (dd, $J_{5,7}$ 13.3, J_{PH} 6.2 Hz, H^7); H^8 and Me obscured; $^{31}P\{^1H\}$ (C_7D_8), AMX (X = ^{103}Rh): P^A 212.4 (dd, $^1J_{RhP}$ 256, $^2J_{AM}$ 7.3 Hz); P^M 203.3 (dd, $^1J_{RhP}$ 261 Hz); ligand (^1H) 4.7—4.4 (m, POCHMe$_2$), 1.9—1.5 (m, PCH_2CH_2P), and 1.4—1.0 (m, POCHMe_2).

complexes (**5a**) and (**5b**) were identical to those of the genuine derivatives prepared from $[(\eta^3\text{-1-MeC}_3H_4)Rh(cod)]$[15] (cod = cyclo-octa-1,5-diene) and $(Pr^iO)_2PCH_2CH_2P(OPr^i)_2$.

We are at present investigating the mechanism of these reactions in detail, and extending this study to other diene substrates. However, it is clear even at this stage that there is a fundamental difference in the reaction of buta-1,3-diene with the two binuclear rhodium hydrides (**1**) and (**2**). With the former, two equivalents of butadiene are required: the first equivalent dehydrogenates (**1**) to generate but-2-ene (*cis–trans*-mixture by ^1H n.m.r.) and some unknown, transitory species which reacts rapidly with another equivalent of butadiene to generate (**3**); in the latter reaction, only one equivalent of buta-1,3-diene is necessary to generate the initially observed but-1-enyl-hydride complexes (**4a**) and (**4b**). These reactions emphasise the ability of donor atom substituents [Pr^i in (**1**) *vs.* Pr^iO in (**2**)] to affect reaction pathways dramatically.

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