Rapid Reversible Fission of a C–H Bond in a Metal Complex: *X*-Ray Crystal Structure of [RhHCl($Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2$)]

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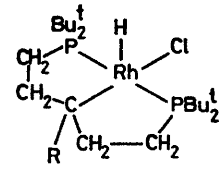
Summary The occurrence and stereochemistry of a rapid reversible C–H fission in [RhHCl($Bu^t_2PCH_2CH_2CHCH_2$-$CH_2PBu^t_2$)] is established by n.m.r. spectroscopy, including triple resonance INDOR, and by *X*-ray crystallography.

There is considerable interest in the interaction of C–H bonds with transition metals in complexes; aliphatic groups are of special interest.[1] Usually C–H fission, if it occurs at all, is slow. We report an example in which it is rapid at or below room temperature.

Treatment of $RhCl_3 \cdot 3H_2O$ with $Bu^t_2P(CH_2)_5PBu^t_2$ in ethanol gives a 16-atom ring hydrido complex [$Rh_2H_2Cl_4$-{$Bu^t_2P(CH_2)_5PBu^t_2$}$_2$]† (*ca.* 50% yield) and the cyclometallated complex [RhHCl($Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2$)] (**1**, R = H) (*ca.* 30% yield), together with small amounts of closely related cyclometallated complexes which have not been characterized. Treatment of [$Rh_2H_2Cl_4${$Bu^t_2P(CH_2)_5$-PBu^t_2}$_2$] with 2-methylpyridine promotes cyclometallation and gives pure (**1**, R = H) in >90% yield. The structure of this complex has been determined by single crystal *X*-ray diffraction. The complex was obtained in two crystalline forms from light petroleum (b.p. 60—80 °C), both of which are monoclinic, space group $P2_1/c$, with $Z = 4$. The α-form has cell dimensions $a = 11{\cdot}906(2)$, $b = 16{\cdot}427(3)$, $c = 13{\cdot}245(2)$ Å, $\beta = 104{\cdot}13(1)°$, while those for the β-form are $a = 12{\cdot}316(3)$, $b = 14{\cdot}373(3)$, $c = 14{\cdot}841(2)$ Å, $\beta = 104{\cdot}82(2)°$. Because of the possibility that these were different isomers we have determined the structures of both forms but find that they both have the same configuration, with the metallated C–H and Rh–H bonds mutually *trans*. The Figure is based on the rather more accurate analysis of the β-form, for which refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms gives a final R of 0·024 for the 3867 F_0 having $I > 3\sigma(I)$. The dimensions of the molecule in the α-form (R = 0·04 for 3125 F_0, with hydrogen atoms as fixed contributions) do not differ significantly.‡



(**1**)

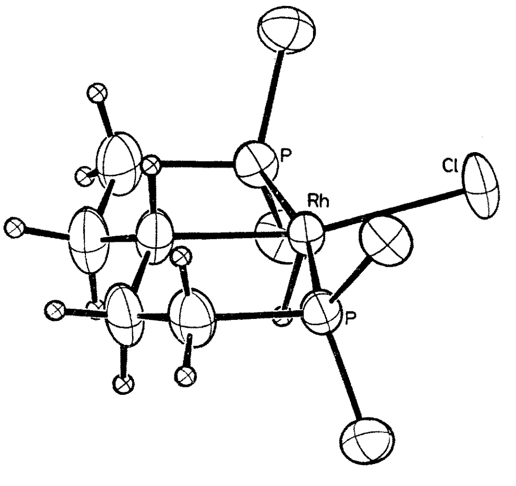


Figure. ORTEP drawing of the molecular structure of [RhHCl($Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2$)]. For clarity, the methyl groups have been omitted and the hydrogen atoms have been assigned artificially low temperature factors of U_{iso} = 0·006 Å^2. Bond lengths to rhodium are: Rh–C, 2·082(2); Rh–P, 2·310, 2·318(1); Rh–Cl, 2·452(1); and Rh–H, 1·36(3) Å.

The cyclometallated hydrido-complex (**1**, R = H) does not show a hydride resonance in its ^1H n.m.r. spectrum at room temperature. However, on cooling a broad resonance starts to appear. At −23 °C it is a broad singlet, at −38 °C a broad doublet (*J ca.* 50 Hz) and at or below −62 °C it is a doublet of triplets, δ_{RhH} −30·1 p.p.m., ^1J(RhH) 55 and ^2J(PH) 19 Hz. We ascribe the non-observance of the hydride resonance at room temperature to the rapid interconversion of (**2**) and (**3**) (Scheme). The interconversion may be concerted (process a) or stepwise with a carbenoid–ylide intermediate (**4**) (process b). We have reported the synthesis and structure of the iridium–carbene complex [IrCl($Bu^t_2PCH_2CH_2CCH_2CH_2PBu^t_2$)],[2] and

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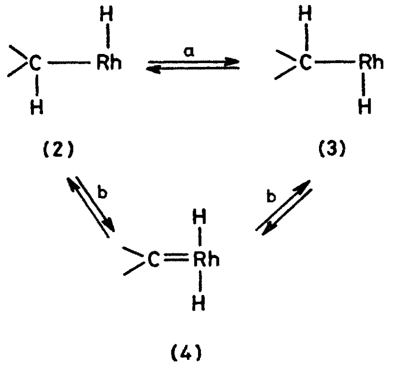
† This and other complexes described here have been characterized by elemental analysis, molecular weight measurements, and n.m.r. and i.r. spectroscopy.

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

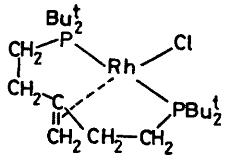


Scheme. (a) Concerted process requiring a transoid arrangement of $\underset{\text{H}}{\text{C}}\text{–}\overset{\text{H}}{\text{Rh}}$ and a vacant orbital on the rhodium atom. (b) Stepwise, or carbenoid (ylide) mechanism.

hydrido–carbene–metal compounds have been postulated as intermediates in reactions.[3,4] If either of the processes a or b shown in the Scheme is correct then one would expect that the rhodium atom would be effectively equally coupled to two hydrogen atoms with an averaged coupling constant. A triple resonance ^1H-$\{^{31}P,^{103}Rh\}$ INDOR experiment at 25 °C, observing one of the two sharp lines of the t-butyl 'triplet,' gave the rhodium resonance as a 1:2:1 triplet [$\Xi(^{103}Rh)$ 3 163 252 Hz], with $J(RhH) = 24$ Hz. Since $^1J(RhH)$ at -62 °C is 55 Hz and the value of $^2J(RhCH)$ will be small and probably opposite in sign[5] the time-averaged coupling of 24 Hz is consistent wih the rapid fluxional processes depicted in the Scheme. Hydrido–alkyl tertiary phosphine–rhodium complexes are probably involved in catalytic reactions of industrial interest, *e.g.* hydroformylation and hydrogenation and a reversible process of the type depicted in the Scheme could occur in such systems.

We know of no other metal complex where alkyl C–H fission is rapid. The dihydrido–methylene–triosmium cluster compound $[Os_3H_2(CH_2)(CO)_{10}]$ has been shown to be in tautomeric equilibrium with the hydrido–methyl complex $[Os_3H(CH_3)(CO)_{10}]$ in the very interesting studies of Shapley *et al.*[4] The rate constant (methyl → methylene), however, is only *ca.* 10^{-3} s^{-1} at 14 °C. This process must therefore be much less rapid than is the case with our system.

We have also treated $RhCl_3{\cdot}3H_2O$ with $Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2$ to give the binuclear complex $[Rh_2H_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2]$ (60%) and some of the cyclometallated complex (**1**, R = Me) contaminated by the olefin–rhodium(I) complex (**5**). Treatment of $[Rh_2H_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2]$ with 2-methylpyridine gave (**1**, R = Me) in 75% yield. The structure of this complex has been established by single crystal *X*-ray crystallography as (**1**, R = Me). As expected, this hydride is not fluxional and at room temperature it shows a well-defined hydride resonance at $-27{\cdot}3$ p.p.m., $^1J(RhH)$ 49 and $^2J(PH)$ 11 Hz. Interestingly it very slowly loses dihydrogen in refluxing propan-2-ol to give the olefin complex (**5**) and the conversion is promoted by a little (*ca.* 10%) water in the propan-2-ol. After a few days conversion was 100% and the isolated yield of pure (**5**) was 96%. The structure of this olefin complex has also been established by *X*-ray crystallography.



(5)

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