The Activation of C–H Bonds in Cyclopentane by Bis(phosphine)rhenium Heptahydrides

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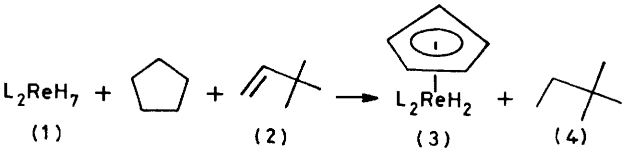
Summary In the presence of 3,3-dimethylbut-1-ene, the complexes L_2ReH_7 ($L = PPh_3$ or PEt_2Ph) dehydrogenate cyclopentane, giving the dihydrido-cyclopentadienyl compounds $L_2(\eta^5\text{-}C_5H_5)ReH_2$.

The activation of sp^3 C–H bonds by transition metal complexes under mild conditions has been widely observed in the case of co-ordinated molecules (phosphines and olefins).[1,2] Intermolecular cleavage of sp^3 C–H bonds is, however, much less common and is essentially limited to activated Me–X molecules (X = Ar, CN, CO_2R, *etc.*).[3,4] Apart from the Pt^{II}-catalysed H/D exchange reactions of alkanes,[2,5] in which no organometallic intermediates have been isolated, the only known examples of intermolecular cleavage of apparently non-activated sp^3 C–H bonds by transition metal complexes seem to be those found recently by Green[3] (insertion of tungstenocene into a C–H bond of tetramethylsilane) and Crabtree *et al.*[6] [dehydrogenation of cyclopentane and cyclo-octane by a cationic bis(phosphine)iridium complex, giving $L_2(\eta^5\text{-}C_5H_5)IrH^+$ and $L_2(\text{cyclo-octa-1,5-diene})Ir^+$, respectively]. Here we report that the bis(phosphine)rhenium heptahydrides (**1a**) and (**1b**) activate the C–H bonds in cyclopentane under very mild conditions (Scheme 1).

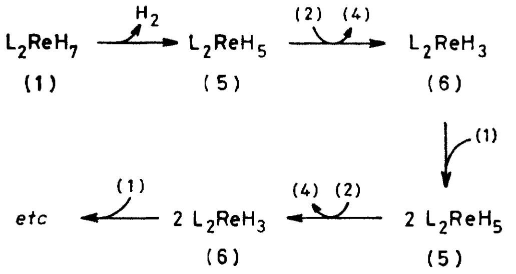


a; $L = PPh_3$
b; $L = PEt_2Ph$

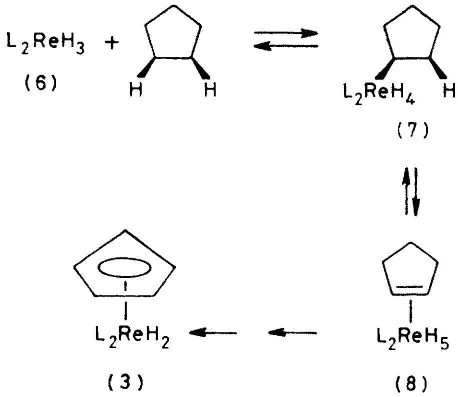
Scheme 1

The reaction of (**1a**) with either cyclopentadiene or cyclopentene gives the cyclopentadienyl dihydride (**3a**)[7]† We have now found that the same dihydride (**3a**) is formed from (**1a**) and cyclopentane when the olefin (**2**) is added as a hydrogen acceptor[6] Thus, (**3a**) was formed in 25% yield (by ^{1}H n m r , 10% isolated yield) when 200 mg of (**1a**) and 0 36 ml of (**2**) were refluxed (in a closed system) in 10 ml of cyclopentane, at most, a trace [$<$ 0 2 mol per mol of (**1a**)] of dihydrogen was evolved and *ca* 4 5 mol of 2,2-dimethylbutane (**4**) (by g l c) were formed per mol of (**1a**) The only observable hydride resonances in the final reaction mixture were those of (**3a**) Similarly, at 80 °C (sealed tube), the heptahydride (**1b**)[8] gave (**3b**) in 15% yield (by ^{1}H n m r), (**3b**) was also prepared (oil, 70% yield) from (**1b**) and cyclopentadiene {τ [$(CD_3)_2CO$] 2 6 (10 H, m, Ph), 5 6 (5 H, s, η^5-C_5H_5), 8 2 and 9 1 (20 H, m, Et), and 22 0 (2 H, t, *J* 40 Hz, ReH_2)} No cyclopentadienyl dihydride (**3**) was formed from cyclopentane in the absence of the hydrogen acceptor (**2**)

The mechanism of this dehydrogenation is not entirely clear In the presence of the olefin (**2**), the spontaneous loss of dihydrogen from only a small fraction of the heptahydride (**1**) may be sufficient to trigger its complete trans formation by (**2**) into the 16e and 14e species (**5**) and (**6**) (Scheme 2) The latter can, presumably either undergo further dehydrogenation by (**2**) to an as yet uncharacterised rhenium species or insert into a C–H bond of cyclopentane (Scheme 3) β-elimination would then lead to the η^2-cyclopentene intermediate (**8**), further dehydrogenation of which affords (**3**)[7] We think the observed dehydrogenation of cyclopentane is due to the imposed synperiplanar relationship of the C–H and C–Re bonds in an intermediate such as (**7**), rather than to any exceptional intrinsic reactivity of the C–H bonds in cyclopentane which might favour the insertion reaction (**6**) → (**7**) Such a synperiplanar relationship has been shown[9] to be a requirement for facile β-elimination and it may be that this makes the reaction (**7**) → (**8**) fast enough to compete with reductive elimination (**7**) → (**6**) and the further dehydrogenation of the hydride (**6**) Experiments with deuteriated species are in progress to verify this and it is interesting in this connection to recall that the heptahydride (**1b**) undergoes H/D exchange with [$^{2}H_6$]benzene in a closed system at 100 °C[8]



Scheme 2



Scheme 3

We thank the Compagnie des Métaux Précieux for a loan of rhenium

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† *Added in proof* the chemical shift (τ 25 5) reported in ref 7 for the hydride resonance in (**3a**) is erroneous, the correct value is τ 20·5

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