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METAL HYDRIDE REDUCTION OF SOME σ- AND π-ALLYL AND BENZYL DERIVATIVES OF MERCURY AND PALLADIUM

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SUMMARY

The reduction of 2-butenyl–mercuric (crotyl–mercuric) systems, RHgX where X=Cl, Br, $OCOCH_3$, by sodium borohydride and trimethyltin hydride has been investigated and under all conditions examined, 1-butene is the sole organic product. Crotylmercuric hydride seems likely to form and then to undergo either intramolecular transfer of hydrogen from mercury to carbon in an S_Ni' manner, or S_N2' displacement of mercury by some hydride species leading to 1-butene, or reactions producing crotyl–Hg^I or crotyl–Hg^- which are cleaved by water or methanol to again yield 1-butene. π-Crotylpalladium chloride on reduction yields only *trans*-2-butene, but in the presence of increasing concentrations of triphenylphosphine, which promotes the $\pi \rightleftharpoons \sigma$ equilibrium of allylpalladium chloride systems, substantial amounts of 1-butene are formed.

In aqueous tetrahydrofuran, sodium borohydride converts benzylmercuric chloride cleanly to dibenzylmercury. Reduction by tetramethylammonium borohydride in benzene, yields toluene (70%) and dibenzylmercury (30%) whereas toluene was the only product from trimethyltin hydride reduction.

INTRODUCTION

There has been considerable recent interest in the mechanisms of metal hydride reductions of carbon–metal systems[1-4] and the oxymercuration–borohydride demercuration sequence for the functionalisation of alkenes[5] certainly has stimulated a good part of this activity. Other reasons, such as specific deuterium-labelling via reduction of C–M bonds[6], are also important. There appears to be rather general agreement[2-4] that radical mechanisms are most successful in relationalising the results for metal hydride reduction of alkyl–mercury systems. On the other hand, reduction of certain C–Pd bonds seemed to be too specific for radical intervention, and intramolecular movement of hydrogen in an organopalladium hydride intermediate was postulated[7].

Our interest in this area was prompted by the discovery of the remarkably specific symmetrisation of benzylmercuric chloride by $NaBH_4$ in aqueous THF, and

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we extended the study to the related crotyl–, cinnamyl– and indenyl–mercury systems. Our conclusions for the σ-crotylmercuric systems encouraged examination of π-crotylpalladium compounds, since these could be equilibrated, under the proper conditions, with their σ counterparts. Such changes in the nature of the organopalladium species had predictable consequences, regarding product distributions, if our ideas were sound.

Some years ago, Sleezer[27] had identified the hydrocarbon products found in the reduction of some allylmercury compounds by sodium borohydride, lithium aluminium hydride and sodium amalgam, but the mechanisms suggested were very tentative, particularly since D-labelled reducing agents and solvents were not employed.

RESULTS AND DISCUSSION

Reduction of trans-CH_3–CH=CH–CH_2HgX

The reactions of *trans*-2-butenylmercuric chloride, bromide or acetate, either as suspensions in water, or under homogeneous conditions in aqueous THF, with $NaBH_4$ are extremely rapid at room temperature, and lead to mercury formation. On the basis of GLC and careful direct PMR examination (100 MHz) of products, the organic product is essentially exclusively 1-butene. Reduction of the chloride (in THF-d_8) with trimethyltin hydride (added neat) again yielded l-butene (and trimethyltin chloride).

It is most illuminating to compare this remarkable specificity with results reported for other reactions where butenyl radicals almost certainly are intermediates. This comparison is prompted by recent reports[2–4] in which reduction (by $NaBH_4$ or R_3SnH) of alkylmercuric halides or acetates is considered to involve alkyl radicals. Walling and Thaler's[8] studies of the free-radical allylic chlorination of the butenes with tert-butyl hypochlorite are especially pertinent and demonstrate (*i*), that 2-butenyl products are favored by wide margins irrespective of whether 1-butene or (*cis* or *trans*)-2-butene is the reactant, and (*ii*), that allylic radicals are configurationally stable. Subsequently Menapace and Kuivila[9] reported on the R_3SnH reduction of the *cis* and *trans* crotyl and α-methallyl chlorides, and again 2-butene was the predominant product, irrespective of allylic chloride reactant. R_3SnH reductions of organic halides are generally agreed to involve organic radicals[9,10].

The exclusive formation of 1-butene in these reductions is difficult to reconcile with the above reports, if butenyl radicals are indeed involved in our reactions. On the assumption that the form(s) the butenyl radical may take are essentially identical irrespective of precursor* [*i.e.* tert-butyl hypochlorite and butene[8]; R_3SnH and crotyl chloride[9]; and crotylmercuric chloride and BH_4^- or R_3SnH(?)] the vastly different product distribution in the present case would be due to substantial differences in the transition state for the H abstraction leading to product. Since halogen and hydrogen abstraction (from R_3SnH) are expected to be quite exothermic, the transition state for both will resemble a radical, with little bond formation. Comparisons made by Kuivila and Menapace[9] seem to support this. Hence in the present case, there seems no reason

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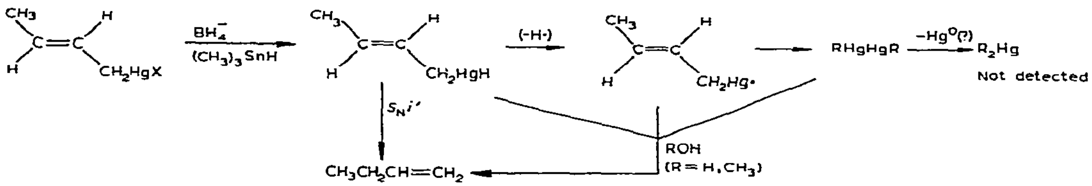
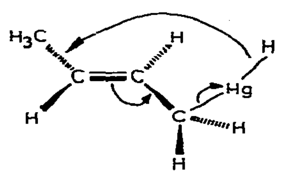
* This appears reasonable for a stabilised (and comparatively long-lived) allyl radical, and comparisons[9] for previous reactions seem to support this.

to postulate grossly different positions for the transition state along the reaction coordinate since in the $(CH_3)_3SnH$ reduction (in which Sn–H would almost certainly be the H donor) the situation must be nearly identical with R_3SnH reduction of crotyl chloride, as regards the transition state for H abstraction. It therefore seems highly unlikely that butenyl radicals are involved in the $(CH_3)_3SnH$ or BH_4^- reduction of crotyl mercurials. Without evaluating the data in great detail, the known behaviour of butenyl carbonium ions[11] and carbanions[12] suggests strongly that neither can account for exclusive 1-butene formation.

We suggest that BH_4^- or $(CH_3)_3SnH$ convert the crotylmercuric halide or acetate to hydride, as has been previously postulated for alkyl mercury systems[1,2,4]. Formation of 1-butene can be envisaged to arise from this intermediate in a number of ways, depending on solvent (*vide infra*).



Rapid intramolecular collapse of the hydride can be envisaged to proceed in the S_Ni' manner drawn below, and which has some analogy with the neutral demercuration of crotylmercuric acetate in acetic acid[13].



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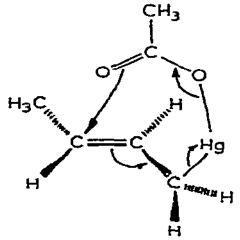
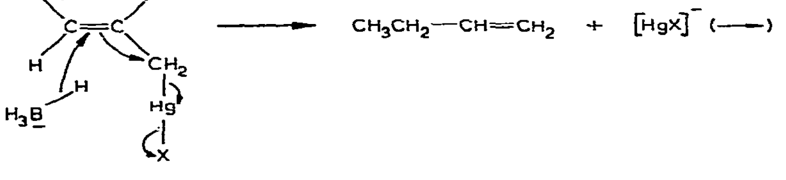
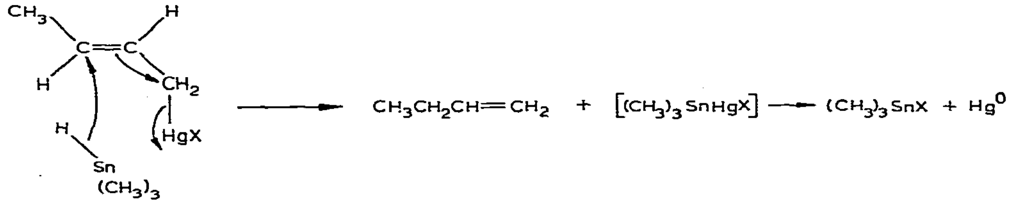


However, assuming a linear (or even slightly bent) C–Hg–H system, in the most favored ground state conformation (presumably that one maximising σ–π conjugation) the hydrogen is well-removed (≈4–5Å) from the remote carbon of the double bond. Substantial bending and deformation of bonds about mercury would be required on passing to a feasible transition state, but it is unclear how difficult this might be for weak heavy-atom centered bonds. In the case of crotylmercuric acetate above, the carbonyl system can be nicely positioned for bond formation.

Hence, it is necessary to consider the operation of an S_N2' pathway as drawn below, particularly in the case of BH_4^-.



However, hydride availability from $(CH_3)_3SnH$ seems less likely, and a concerted type of reaction may be possible.



Although reduction with $NaBD_4$ (in D_2O) led to 100% D-incorporation in the product located exclusively at C_3, the fact that $NaBH_4$ required either H_2O or D_2O for solubilising purposes, demands consideration of other mechanisms where protic species may intervene. Thus D-incorporation in the 1-butene (at C_3) does occur when deuterated solvents are employed. For example, reduction with $NaBH_4$ in D_2O/THF (1/5) led to 1-butene with *ca.* 70% D-incorporation at C_3. [In 3-deutero-1-butene, the CH_3 signal appears as a doublet of triplets due to vicinal H–H (J 7Hz) and H–D (J 1.2 Hz) coupling. (Fig. 1)]. $NaBD_4$ in H_2O/THF (1/5) led to no D-incorporation in the exclusively 1-butene. The differences here could be due to isotope effects, but establish solvent participation to a marked degree. However, in the first case approximately 30% of hydrogen derives from the BH_4^- and the S_Ni' mechanism is probably in action to that extent, since BH_4^-–D_2O exchange would not be significant under these conditions[14], and the reduction reaction is extremely rapid. This solvent

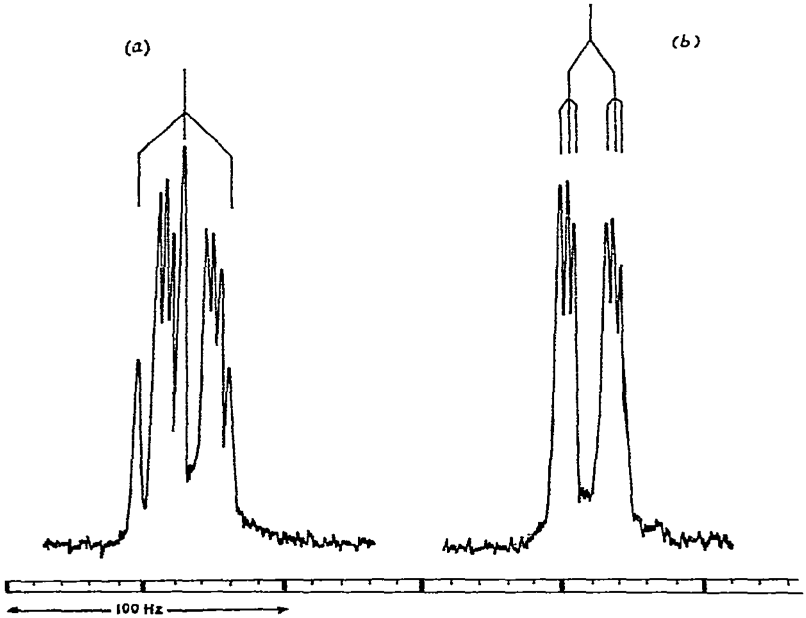


Fig. 1. 100 MHz spectra (CCl_4) (sweep width 270 Hz) of (*a*) Mixtures of CH_3–CH(D)CH=CH_2 and CH_3-CH_2CH=CH_2 showing vicinal CH_3–CH and CH_3–CD coupling. (*b*) Pure CH_3CH(D)–CH=CH_2 showing only vicinal CH_3–CD coupling.

intervention prompted study of water/methanol systems for $NaBH_4$, in which 1-butene was again the sole product. Thus reduction of crotylmercury chloride by $NaBH_4$ in H_2O/CD_3OH (1/20) led to no D-incorporation, while in H_2O/CH_3OD (1/20) *ca.* 58% D-incorporation at C_3 was observed. These results argue against H atom abstraction from solvent, since in the methanol case H-abstraction from CH_3–OH is favored over CH_3OH abstraction by almost 10–15 kcal/mole[15]. The results point to the solvent (either H_2O or CH_3OH) being a formal proton source*.

It is unclear whether protic solvent intervenes at the hydride or some later stage, since a number of crotylmercury species could conceivably be involved, *i.e.* RHgH, $RHg^{\bullet}$, RHgHgR, R_2Hg or RHg^-. The rapidity of the reaction (with H_2O or CH_3OH) appears to rule out dicrotylmercury from consideration, since diallylmercury and other bisallylic mercurials are relatively stable toward water and alcohols[17,18]. We believe that crotylmercury radical, crotyl–Hg^I or perhaps more likely, crotyl–Hg^- are plausible candidates for exhibition of this extraordinary sensitivity (for organomercurials) toward water and methanol, since electrophilic attack on these sub-valent species should be more facile**. The postulation of crotylmercury(I) or crotyl–Hg^- is reasonable since in the reduction of benzylmercuric chloride with BH_4^- in aqueous THF, dibenzylmercury is the sole product (*vide infra*), and reasonable mechanisms involving analogous species can be written. It is known that electrophilic cleavage of benzyl lags behind allyl[19]. The product, 1-butene, whether it be derived from RHg, RHg^I or RHg^- (R=*trans*-crotyl) on reaction with protic solvent, necessitates the invocation of the S_E' type of cleavage mechanism.

Reduction of cinnamylmercuric bromide

The reduction with $(CH_3)_3SnH$ (in THF-d_8) and $NaBH_4$ (in aqueous THF 1/5) both led to instantaneous mercury formation and organic products consisting of 94% allylbenzene and 6% β-methylstyrene. These distributions agree with those reported by Pasto and Gontarz[2], who suggested the intermediacy of a cinnamyl radical, derived from cinnamylmercuric hydride. Unfortunately there seems to be no information concerning the product distribution for a reaction definitely involving cinnamyl radicals. It is tempting to suggest that S_Ni' decomposition and S_E' cleavage (under protic conditions) of sub-valent cinnamyl–Hg species may be operative, but the presence of phenyl conjugation could be an impediment to allylbenzene formation by these routes depending on transition state details. Reduction by BH_4^- in THF/D_2O (5/1) led to predominantly allylbenzene, however, containing *ca.* 60% D at C_3. This again seems best explained by solvent cleavage of possibly cinnamyl–Hg^I or cinnamyl–Hg^-. Given the presumed stability of cinnamyl radical and the poor H atom donor ability of borohydride and water, it is surprising that no dicinnamyl was formed. However, it may be that cinnamyl radicals rapidly abstract from [HgH] species, since heavy metal atom–hydrogen bonds are notoriously weak. In this case, if the transition state for H abstraction resembles radical, the predominance of allylbenzene is understandable.

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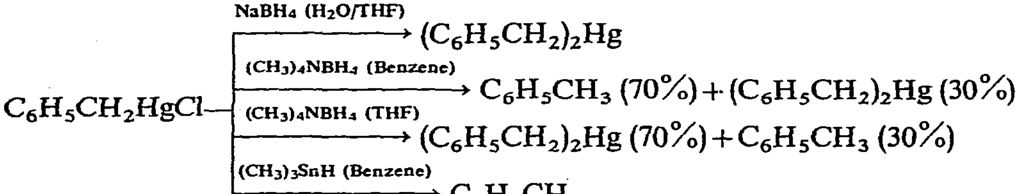
* It has been demonstrated[16] that crotylmercuric chloride is cleaved by HCl to yield entirely 1-butene (with DCl, yields 3-deutero-1-butene) but we showed that the solvent systems employed led to no cleavage of starting material in the very short times prior to addition of reducing agent.

** Certain aspects of the chemistry of RHg^- species have been exposed by F. R. Jensen. See ref. 19.

Reduction of benzylic mercurials

Direct NMR observations (using THF-d_8 as solvent) of the reduction of benzylmercuric chloride [$\delta(CH_2)$ 2.80; $\delta(C_6H_5)$ 7.20 ppm (broad) $J(CH_2\text{–}Hg)$ 264 Hz] by an equimolar amount of $NaBH_4$ in H_2O confirmed dibenzylmercury [$\delta(CH_2)$ 2.45; $\delta(C_6H_5)$ 6.70 ppm (broad); $J(CH_2\text{–}Hg)$ 144 Hz] as the sole organic product. In contrast, reduction by $(CH_3)_4NBH_4$ (solubilized in CD_3OD) in benzene yielded toluene (70%) and dibenzylmercury (30%) while the same agent in THF-d_8 gave dibenzylmercury (70%) and toluene (in addition to $(CH_3)_4N^+Cl^-$). $(CH_3)_3SnH$ in benzene yielded only toluene.



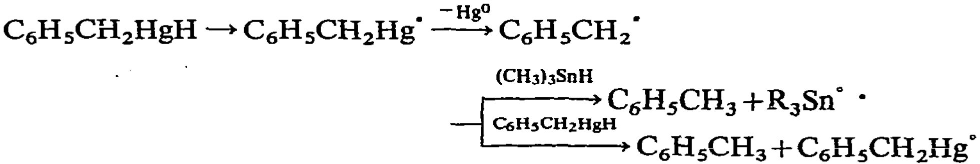
$$C_6H_5CH_2HgCl\left\{\begin{array}{l}\xrightarrow{NaBH_4\ (H_2O/THF)}(C_6H_5CH_2)_2Hg\\ \xrightarrow{(CH_3)_4NBH_4\ (Benzene)}C_6H_5CH_3\ (70\%)+(C_6H_5CH_2)_2Hg\ (30\%)\\ \xrightarrow{(CH_3)_4NBH_4\ (THF)}(C_6H_5CH_2)_2Hg\ (70\%)+C_6H_5CH_3\ (30\%)\\ \xrightarrow{(CH_3)_3SnH\ (Benzene)}C_6H_5CH_3\end{array}\right.$$

The clean symmetrisation by BH_4^- in aqueous THF seems explicable in terms of the following, again assuming intermediacy of RHgH.

$$C_6H_5CH_2HgH\rightarrow C_6H_5CH_2Hg^{\cdot}\rightarrow C_6H_5CH_2HgHgCH_2C_6H_5\xrightarrow{-Hg^0}(C_6H_5CH_2)_2Hg$$

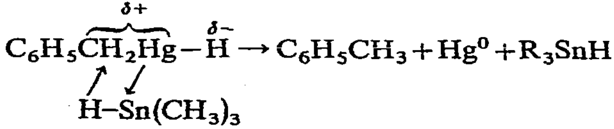
THF and H_2O coordination, as well as possible transfer of spin density onto the benzyl group may confer sufficient stability on $C_6H_5CH_2Hg^{\cdot}$ to favor the coupling reaction and prevent homolysis to yield benzyl radical. Russian workers[20] have also investigated the $NaBH_4$ reduction of several RHgCl compounds and in the case of benzyl mercuric chloride (in dioxan) dibenzylmercury as well as benzyl chloride were formed, but apparently no toluene. However, the very harsh conditions employed (temperatures of 150°) could lead to a number of secondary products (*e.g.* dibenzyl from dibenzylmercury)[21].

Exclusive formation of toluene by $(CH_3)_3SnH$ reduction in benzene could be explained by formation of $C_6H_5CH_2^{\cdot}$ (no solvent stabilisation of $C_6H_5CH_2Hg^{\cdot}$) followed by abstraction from either $(CH_3)_3SnH$ or $C_6H_5CH_2HgH$:



$$C_6H_5CH_2HgH\rightarrow C_6H_5CH_2Hg^{\cdot}\xrightarrow{-Hg^0}C_6H_5CH_2^{\cdot}\left\{\begin{array}{l}\xrightarrow{(CH_3)_3SnH}C_6H_5CH_3+R_3Sn^{\cdot}\\ \xrightarrow{C_6H_5CH_2HgH}C_6H_5CH_3+C_6H_5CH_2Hg^{\cdot}\end{array}\right.$$

Hexamethylditin could then be anticipated as a final product[10] in the first case but none was detected. Bimolecular non-radical mechanisms between $C_6H_5CH_2HgH$ or more likely between $C_6H_5CH_2HgH$ and $(CH_3)_3SnH$ (in excess) deserve consideration also.

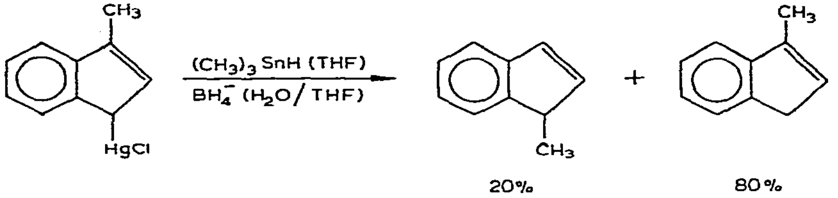


$$C_6H_5\overbrace{CH_2Hg}^{\delta+}-\overset{\delta-}{H}\rightarrow C_6H_5CH_3+Hg^0+R_3SnH$$
$$H\text{–}Sn(CH_3)_3$$

$(CH_3)_4NBH_4$ is less specific in its action, although dibenzylmercury is favored in THF and toluene in benzene solution.

Reduction of (3-methylindenyl)mercuric chloride

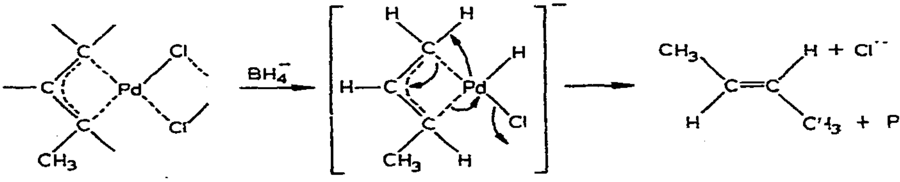
Reduction with $NaBH_4$ (aqueous THF) or $(CH_3)_3SnH$ (THF) produced a mixture of 1-methylindene (20%) and 3-methylindene (80%). No symmetrised products were observed. Since 1-methylindene was demonstrated not to isomerise to the thermodynamically more stable 3-methyl isomer under the reaction conditions, the S_Ni' mode of decomposition of a presumed indenylmercuric hydride intermediate is not the dominant pathway. Also, from consideration already presented concerning transition states for H-abstraction, 1-methylindene would be predicted to be predominant for a radical reaction, since its radical precursor (if a reasonable approximation to the transition state) would be favored. The mechanism of this reduction is not clear, but concerted collapse (S_Ni) could be involved.



Reduction of π-crotylpalladium chloride

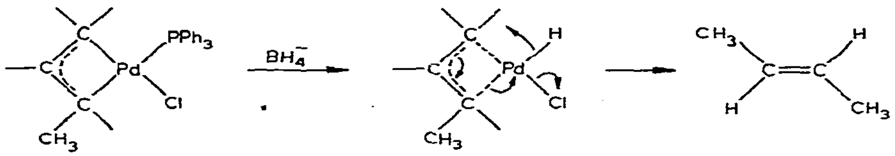
Reduction of π-crotylpalladium chloride by $NaBH_4$ in H_2O/THF media led to the quantitative formation of 2-butene. The presence of one isomer was confirmed by GLC and infrared analysis (CCl_4) showing bands at 3020 cm^{-1} (=CH stretching) and 962 (s) =C–H (out of plane bending). The absence of a C=C stretching vibration between 1600 and 1700 cm^{-1} is consistent with the presence of the symmetrical *trans*-2-butene.

We suggest the intermediacy of a crotylpalladium hydride intermediate which (probably) suffers intramolecular collapse. Vedejs and Salomon[7] have reported highly stereospecific reductions of σ-bonded organopalladium compounds, and also suggested intramolecular movement of hydride from palladium to carbon. In the present case, the incoming hydride could occupy a fifth coordination position at palladium[22] or rupture the chloro-bridged dimer, in either case forming an anionic π-allyl–palladium system, examples of which have been thoroughly characterized[28]. For simplicity of discussion we will assume that palladium remains four coordinate, and that the incoming hydride is located *trans* to the C–CH_3 group in the square plane, as is the well known bridge splitting ligand $(C_6H_5)_3P$ in the monomeric π-crotyl–PdCl·$(C_6H_5)_3P$[23,24]



Migration of H to the primary carbon is clearly favored on proximity grounds, and also if the displacement of the [PdCl] fragment from carbon has any "S_N2 character".

The reduction of the monomeric triphenylphosphine complex of π-crotylpalladium chloride again produced only *trans*-2-butene. This would seem to suggest that H^- from BH_4^-, replaces the $(C_6H_5)_3P$ ligand, to place the H ligand within a feasible distance of the primary carbon for subsequent transfer*.

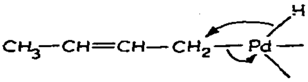


The starting phosphine complex is known to have the gross structure indicated[23,24], with the π-crotyl structure being only very slightly perturbed, allowing no stereochemical leakage in the product.

However, in the presence of two moles of triphenylphosphine, π-crotyl–PdCl dimer is known to be substantially (at least) in the σ-form as shown below[23,24].

with the equilibrium being very heavily in favor of the primary isomer. (Nothing is implied however about the *cis* or *trans* nature of the ligands in the square plane in the σ forms).

Reduction of the above system leads to 55% 2-butene and 45% 1-butene, and it seems reasonable to suggest the origin of 1-butene to be S_Ni' decomposition of a primary σ-crotylpalladium hydride, as outlined for the mercury system. Decomposition as below could account for the 2-butene, which in many ways is similar to the proposals outlined above for the π-crotylpalladium hydride composition.



Clearly S_Ni' decomposition of the secondary α-methallylpalladium hydride species would produce 2-butene, but it seems difficult to postulate a substantial concentration of it, in view of what is known of the equilibrium positions for mobile crotyl–metal systems.

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* However, it is possible that hydride displaces chloride initially, to yield a neutral complex, with hydride *cis* to the C–CH_3 group. Isomerisation, involving interchange of the hydride and $(C_6H_5)_3P$ in the square plane, could subsequently occur (possibly via a five coordinate anionic dihydrido species) to again place hydride *cis* to the primary (–CH_2) carbon. We thank Dr. M. A. Bennett for discussions on this point.

We cannot positively rule out radical mechanisms in these latter cases, and several pathways may be operative.

EXPERIMENTAL

All organomercury compounds have been described elsewhere and had properties identical with those reported[25,26].

Trimethyltin hydride was prepared by the addition of a twenty fold excess of $NaBH_4$ to trimethyltin chloride dissolved in dry diglyme, b.p. 60–61° (lit.[27] 60–61°).

π-Crotylpalladium chloride and its triphenylphosphine complex had properties identical with those previously reported[23,24].

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