Reversible Thermal Carbon–Hydrogen Bond Cleavage in Alkanes and Arenes with Dihalogenobis(triphenylphosphine)palladium(II) Complexes

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Dihalogenobis(triphenylphosphine)palladium(II) complexes **1**, $PdX_2(PPh_3)_2$ (X = Cl, Br, I), reacts reversibly with saturated and aromatic hydrocarbons RH (RH = *p*-xylene, toluene, benzene, *n*-hexane, cyclohexane), slowly at ambient temperature and rapidly on heating at 70–130 °C, to produce hydridodihalogeno(organo)bis(triphenylphosphine)palladium(IV) complexes **2**, $Pd(H)(R)X_2(PPh_3)_2$; in the presence of bases complexes **2** eliminate hydrogen halide forming organobis(triphenylphosphine)palladium(II) halide **3**, $Pd(R)X(PPh_3)_2$.

The activation of C–H bonds in saturated and aromatic hydrocarbons has been of interest in the last decade.[1–11] Complexes of palladium play a significant role in these processes.[3–7] The formation of organopalladium compounds is assumed to be the key step in the catalytic oxidative trifluoroacetoxylation of methane[3] and adamantane,[4] and in the oxidative carboxylation of benzene[5] and cyclohexane.[6] Despite this, the palladation of hydrocarbons has not been investigated extensively, although the cyclopalladation of organic amines, phosphines and sulfides has been studied.[12,13] Only a few examples of the synthesis of bis(σ-aryl)tripalladium(II) complexes *via* the deprotometallation of arenes are known.[7]

The palladation reaction is usually considered to be an electrophilic process[1–7,13] and is carried out in highly polar, low nucleophilic media.[2–7] The nucleophilic behaviour of palladium(II) complexes towards aromatic C–H bonds has also been discussed.[13] This might involve the formation of hydridoorganopalladium(IV) intermediates.[14] We have achieved the activation of saturated and aromatic hydrocarbons using dihalogenobis(triphenylphosphine)palladium(II) complexes in low polarity media. The reaction appears to involve the oxidative addition of metal complexes to the $C(sp^3)$–H bond of hydrocarbons, described first by Bergman and Graham for organoiridium(I) compounds.[9] The palladations were carried out in the liquid hydrocarbon using bis(triphenylphosphine)palladium(II) dihalogenides **1** [eqn. (1)].

$$\underset{\mathbf{1}}{PdX_2(PPh_3)_2} + R\text{–}H \rightleftharpoons \underset{\mathbf{2}}{\{RPd(H)X_2(PPh_3)_2\}} \qquad (1)$$

$$\mathbf{2} \xrightarrow{-\,HX} \underset{\mathbf{3}}{R\text{–}PdX(PPh_3)_2} \qquad (2)$$

In a typical experiment, the hydrocarbon (1 ml) and complex **1** (0.01 mmol) were placed in a glass tube. Following degassing, the tube was filled with argon and sealed. Usually, the reactions were carried out at 70–130 °C; the reaction proceeds slowly at ambient temperature. The amount of organopalladium product was determined as the amount of organic halide RBr or RI by GLC, after adding bromine or iodine solution in tetrachloromethane and internal standard to the cooled contents of the tube. Organopalladium complexes are known to be cleaved quantitatively with halogens.[15] Results for the palladation of saturated, alkylaromatic hydrocarbons and benzene with complexes **1a–1c** under various conditions are listed in Table 1.

The resulting solutions of compounds **2** in hydrocarbons show behaviour typical of the hydrido organo transition metal complexes. They form one equivalent of chloroform in the presence of carbon tetrachloride,[17] and give the corresponding methyl ketones RCOMe after treatment with acetyl chloride, and the acetates $MeCO_2R$ with sodium acetate.

Even after prolonged heating of reaction mixtures only small traces of the product R_2 of the oxidative dimerization of the hydrocarbon RH were found. Therefore, neither complex **3**† nor the diorganopalladium complexes $PdR_2(PPh)_2$, which decompose easily to produce the dimer R_2,[15] are formed to a significant extent. The high thermal stability of *n*-alkylpalladium(IV) complexes has been pointed out several times.[18]

In contrast, the presence of inorganic bases in the reaction mixtures, which irreversibly bind hyrogen halide according to eqn. (2), leads to high yields of complexes **3**. The benzyl complexes **3**, which have the same physical properties as previously reported,[19] could be isolated only after treatment of a homogeneous reaction mixture with potassium carbonate. Diorganopalladium complexes are formed in the presence of inorganic bases too, followed by the rapid precipitation of palladium metal and the accumulation of the product R_2 of the oxidative dimerization of the hydrocarbon substrate RH (see Table 2).

In the case of benzylic derivatives, attempts to isolate the organo-paladium(IV) hydride **2** in pure form led to starting complex **1** only. Hydrido(cyclohexyl)dibromobis(triphenylphosphine)palladium(IV) and the analogous iodide complex could be isolated owing to their low solubility in the reaction medium, in admixture with the starting compound **1**. The solid mixture of compounds **1** and **2** decomposes after several hours at ambient temperature to produce *cis*- and *trans*-isomers of **1** and cyclohexane, as shown by ^1H and ^{31}P NMR spectroscopy and elemental analysis. The mixtures of compounds **1b** and **2b** (R = Cy), containing 10–50% of complex **2b** (according to halogenolysis data and NMR spectroscopy) were characterized by means of IR and ^1H NMR spectroscopy. The appearance of a weak IR absorption band at 2190 cm^{-1} (Pd–H stretch) and two bond peaks at δ −6 and −18 (C_6D_6)‡ in ^1H NMR spectra show the presence of a Pd–H bond in those products.[21] Hence, the presence of Pd–H fragments (confirmed by the chemical test with CCl_4) and Pd–C_6H_{11} fragments (confirmed by halogenolysis, acylation and acetoxylation of the solid mixtures) in 1 : 1 ratio (as determined by comparison of NMR and halogenolysis data), and the formation of cyclohexane and starting complexes **1** by

Table 1 Palladation of hydrocarbons RH[a] with $PdX_2(PPh_3)_2$

		Yield[b] of **2** (%) (*t*/min)		
R–H	*T*/°C	**a**; X = Cl	**b**; X = Br	**c**; X = I
p-$MeC_6H_4CH_2$–H	130	13 (40)[c]	32 (5)	—
c-C_6H_{11}–H	130	13 (90)	20 (45)	19 (45)
	100	—	26 (60)	36 (300)
	70	—	33 (360)	—
$PhCH_2$–H	130	6 (60)[d]	20 (30)	17 (15)
	100	—	26 (180)	21 (45)
	85	—	30 (360)	—
	20	—	5 (24 h)	
n-C_6H_{14}	130	10 (40)[e]	17 (40)[e]	19 (300)[e]
Ph–H	130	—	1.5 (60)	—
	120	0.6 (180)		

[a] R–H bond dissociation enthalpies (E_d) in kcal mol^{-1}:[16] (1 cal = 4.184 J) $MeC_6H_4CH_2$–H 76.7; $PhCH_2$–H 88.0; C_6H_{11}–H, 95.6; $Bu^nCH(Me)$–H, 97.0; MeC_6H_4–H, 111; Ph–H, 111. [b] According to GLC determination of halogenodemetallation product RBr or RI, based on palladium. [c] 1 : 1 Mixture of α- and 2-xylyl derivatives. [d] 7 : 1 Mixture of benzyl and tolyl derivatives. [e] Mixture of 2- and 3-hexyl derivatives.

Table 2 Palladation of hydrocarbons RH with $PdBr_2(PPh_3)_2$ in the presence of potassium carbonate, 130 °C

R–H	*t*/min	Yield (%)	
		3[a]	R–R[b]
p-$MeC_6H_4CH_2$–H	8	84	2.0
	50	6	49
c-C_6H_{11}–H	16	25	2.2
	90	11	18
$PhCH_2$–H	8	80	5.4[c]
	60	1.5	46[c]
MeC_6H_4–H	8	11[c]	5.4[c]
	60	4.5[c]	46[c]
Ph–H	60	16	1.5
	270	12	6.3

[a] According to GLC determination of halogenodemetallation product RBr or RI. [b] According to GLC determination. [c] Mixture of isomers.

decomposition of the solids, allow us to ascribe the formula **2** to the products of reaction (1).

To find out more about the mechanism of the reaction, we studied the influence of various factors on its rate. Reaction (1) is first order in each of the reagents involved and is reversible. The rate of reaction (1) was not affected by both oxidants and additives that lead to initiation or inhibition of radical processes such as air, oxygen, benzoquinone, sodium persulfate or hydroquinone. Therefore, the palladation (1) proceeds neither by a radical mechanism nor *via* Pd^0 or Pd^I intermediates. So we can conclude that reaction (1) proceeds *via* the oxidative addition of C–H bonds of hydrocarbons to palladium(II) complexes, the equilibrium of which is shifted to the left even in pure hydrocarbon media. This is an important positive factor for its use in catalytic activation of hydrocarbons.

As shown in Table 1, the reactivity of the palladium(II) complexes decreases in the order **1c** > **1b** > **1a**, as does the nucleophilicity of metal atom. The reactivity of the hydrocarbons increases as their C–H bond energy decreases; so benzene is the most inert substrate. The same factor determines the regioselectivity of metallation both of alkylarenes and *n*-hexane, which contain C–H bonds of different types.§ These results are opposite to the observations of Bergman for iridium(I), rhenium(I) and rhodium(I) complexes[10] and to Whitesides' observations for complexes of platinum(0).[11]

Comparison of the data in Tables 1 and 2 shows that the addition of potassium carbonate changes the regioselectivity of toluene metallation. This appears to result from the formation of the new C–H bond activation reagents in the reaction mixture, palladium(0) complexes or palladium metal, which possess 'normal' selectivity as do the corresponding platinum(0) complexes.[11]

Reaction (1) is, to our knowledge, the first example of the thermal intermolecular palladation of alkanes which proceeds by the insertion of palladium(II) complexes into C–H bonds. The system differs from many previously described metal complex systems, which are able to add alkanes oxidatively.[9–11] In our system the hydridoorgano complex is formed from the 'inorganic' precursor, which does not require photochemical activation. The problem of whether or not the synthesis of π-allylpalladium(II) complexes by alkene metallation with palladium(II) salts proceeds *via* allylhydridopalladium(IV) intermediates,[22] and similar questions relating to C–H bond activation reactions,[14] may be closer to a solution.

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Footnotes

† Using bromobis(triphenylphosphine)phenylpalladium(II) as a model compound, it was found that its hydrocarbon solutions decompose when heated at 70–130 °C, to form biphenyl and palladium metal.

‡ Because of the broadness of the signals no coupling to the phosphorus nuclei can be observed. The width of the signals in the ^1H NMR spectra (800 Hz, spectra determined on a Bruker MSL instrument at 20 °C) seems to be due to the rapid exchange processes, in which complexes **2** take part and which involve triphenylphosphine ligand dissociation–coordination and cyclohexane reductive elimination–oxidative addition. Both the low stability of complexes and their low solubility do not allow us to confirm this suggestion by analysis of the NMR spectra at lower temperatures. The existence of two signals of near integral intensity may be assigned to two of six possible diastereoisomers of complex **2b**, one with halogen and the other with phosphine ligands *trans* to the hydride. It is known that hydride ligands *trans* to halogen absorb at a higher field than hydride ligands *trans* to a phosphine ligand.[20] The ratio of the integrated intensity of the phenyl and hydride proton signals was in the range from 60 : 1 to 300 : 1, which corresponds to the data for halogenolysis of mixtures of **1b** and **2b**, containing from 50% to 10% of **2b**.

§ This result appears to be due to the observed free energy loss for palladium(II) insertion into the C–H bond. Thus, the reaction between cyclohexane and the dibromobis(triphenylphosphine)palladium(II) complex is characterized by free energy $\Delta\Delta G = 2.5$ kcal mol^{-1} and $\Delta\Delta H = -2.1$ kcal mol^{-1} at 100 °C (not statistically corrected; 1 cal = 4.184 J). It forces the palladium atom to 'choose' the weakest C–H bonds in hydrocarbons, *e.g.* secondary bonds in *n*-hexane.

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