Russian Chemical Reviews **63** (2) 125 – 138 (1994) ©1994 Russian Academy of Sciences and Turpion Ltd

UDC 541.127

Reactions of hydrocarbons with electrophilic transition metal complexes in trifluoroacetic acid

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Abstract. The results of studies on the catalytic and stoichiometric activation of C–H and C=C bonds in hydrocarbons by electrophilic metal complexes in trifluoroacetic acid are surveyed. Reactions involving the dehydrogenation of cycloalkanes, carboxylation and oxidative carbonylation of alkanes and aromatic compounds, oxidative coupling of aromatic hydrocarbons, oligomerisation of norbornadiene with participation of transition metal trifluoroacetates, and certain others are examined. Much attention is devoted to the conditions for the generation of active species and their nature. The bibliography includes 185 references.

I. Introduction

The reactions of alkanes with participation of transition metal complexes have aroused much interest in connection with the possibility of devising new selective catalytic procedures for the processing of hydrocarbons. Metal complex activation of alkanes was discovered in relation to platinum(II) complexes in 1969.[1] The wide scale study of this process made it possible to elucidate the factors affecting the reactivity of C–H bonds in alkanes and the mechanism of the activation of saturated hydrocarbons by transition metal complexes,[2–5] to extend the range of metal complexes capable of activating alkanes,[6–11] and to discover new reactions of alkanes, including methane.[12–16]

The role of electrophilic metal-containing centres in the catalytic and stoichiometric activation of C=C and C–H bonds in hydrocarbons is discussed in the present review and other reactions, the occurrence of which is favoured by an increase in the electron-accepting capacity of the metal centre, are considered. Data on the functionalisation of alkanes, alkenes, and aromatic compounds in the presence of transition metal complexes in trifluoroacetic acid are summarised. Questions concerning the oxidation of alkyl-substituted aromatic compounds by variable valence metal ions and thallium(III) trifluoroacetate have been dealt with in other reviews,[17,18] the oxidation of other substrates has been examined in a book,[19] and studies on the selective substitution of hydrogen attached to a saturated carbon atom, mainly a tertiary carbon atom, have been surveyed by Boguslavskaya et al.[20]

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Received 9 December 1993
Uspekhi Khimii **63** (2) 130 – 143 (1994); translated by A K Grzybowski

II. Trifluoroacetic acid and transition metal carboxylates as components of catalytic systems

Trifluoroacetic acid (TFA) is usually obtained by the electrolytic fluorination of acetyl chloride or fluoride; the acidity of its aqueous solutions is comparable to that of aqueous solutions of inorganic acids. It is a mild dehydrating but not oxidising agent.

Acid	pK_a	ε
CF_3COOH	0.2	8.4
CH_3COOH	4.76	9.55
HCOOH	3.7	62.0

The low dielectric constant shows that TFA is a poor ionising solvent — ions are solvated in CF_3COOH much less effectively than in water. However, TFA is a convenient solvent for the nitration of aromatic compounds with nitric acid,[21] the bromination of toluene,[22] the synthesis of adamantanol,[23] the hydroxylation of alkanes,[24] and a number of other reactions, and also for the investigation of the kinetics of electrophilic substitution processes. Solutions of mixtures of alkali metal nitrates and chlorides in aqueous TFA can be used for the selective halogenation of aromatic compounds.[25] A series of new oxidation reactions involving H_2O_2 in trifluoroacetic acid,[26,27] including perfluorinated aromatic and olefin compounds, have been discovered.

Metal trifluoroacetates are obtained by the reactions of the corresponding oxides, hydroxides, carbonates, sulfates, and amalgamated metals (in the case of aluminium and magnesium) with TFA,[28] via the oxidative addition of TFA to low-valence complexes,[29] and also by the reactions of metal chlorides (or organometallic compounds) with a solution of CF_3COOAg in organic solvents (nitromethane, acetone).[28,30] A widely used method of synthesis of metal trifluoroacetate complexes involves carboxylate exchange.[28,31,32]

$$Rh_2(O_2CCH_3)_4 + 4CF_3COOH \xrightarrow{k_i} \longrightarrow Rh_2(O_2CCF_3)_i(O_2CCH_3)_{4-i} + iCH_3COOH\ .$$

It has been shown for this reaction that the substitution of the acetate anion by the trifluoroacetate anion is a stepwise process, the ratios of the rate constants for the successive reactions being $k_1 : k_2 : k_3 : k_4 = 1 : 2.0 : 0.1 : 0.025$.

It is known from the totality of the physicochemical properties of carboxylates that the stability of the RCOO–M bond as a rule decreases as the electron-accepting properties of the group R become more marked.[33]

$CH_3 > CH_2Cl > CH_2F$,

$CH_3 > CH_2F > CHF_2 > CF_3$,

$CH_3 >$ Nic > *iso*-Nic,

where Nic = nicotine.

The principal feature of the carboxy-group is the multiplicity of its structural functions; it can play the role of a monodentate, cyclic bidentate, bridging bidentate, tridentate, and even tetradentate ligand with different (*syn* or *anti*) orientations of the bonds with the metal.[33] Monodentate and bridged coordinations are most characteristic of the trifluoroacetate group.[28] Comparatively numerous structural investigations of the carboxylates of 3*d* elements have been carried out hitherto and have made it possible to discover an extremely wide and varied spectrum of structures of these substances and the functional possibilities of the carboxylate ligands.[33,34]

The crystal and molecular structures of palladium acetate, the interest in which is due to its catalytic properties, have been investigated.[35] This substance is a symmetrical trimer $Pd_3(O_2CCH_3)_6$ with double *syn, syn*-bridges between each pair of palladium atoms, which was demonstrated by X-ray diffraction study of its solvates.[35–37] The oxygen atoms surrounding each palladium atom in this compound are arranged approximately in the same plane and give rise to the square configurations usual for d^8 metals. The compound differs sharply from the trimeric carboxylates of d^3-d^6 elements,[33] which must be stabilised by a μ_3-ligand (usually a μ_3-O atom located at the centre of an isosceles triangle comprising three M atoms), and also from platinum acetate, which is a tetramer[38] with strong covalent metal–metal bonds. X-Ray diffraction study of volatile trinuclear palladium(II) carboxylates—$Pd_3(O_2CBu^t)_6$ and $Pd_3(O_2CCF_3)_6$—showed[39] that both complexes are trimers like palladium acetate, but palladium trifluoroacetate has this structure in solution in benzene only at temperatures below 37 °C. The molecular geometries of the complexes are also extremely similar. The observed Pd...Pd distances (3.1–3.2 Å) exceed greatly the usual lengths of palladium–palladium bonds and indicate the absence of valence interactions. The replacement of an electron-donating substituent (CH_3) in the carboxylate ligand by an electron-accepting substituent (CF_3) leads to an increase in the Pd...Pd distance.

Monodentate coordination of the CF_3COO^- anion has been demonstrated by X-ray diffraction for different complexes, including $Pd_2(dppm)_2(O_2CCF_3)_2$[40] and $Pd(dppm)(O_2CCF_3)_2$,[41] where dppm = bis(diphenylphosphinomethane), $M(O_2CCF_3)_2 \cdot (NO)(PPh_3)_2$, where M = Rh or Ir,[42] and $Rh(CO)(O_2CCF_3) \cdot (PPh_3)_2$.[43] Both the monodentate and bridged coordinations of the trifluoroacetate groups have been found in the complex $Pr(O_2CCF_3)_3(H_2O)_3$,[44] which is a centrosymmetrical dimer in the solid state, and in the dimer $[Ru(C_6H_9)P(C_6H_{11})_2]_2 \cdot (\mu\text{-}CF_3CO_2)_2(CF_3CO_2)_2(\mu\text{-}OH_2)_2$.[45]

Vibrational spectroscopic data, determinations of the molecular mass, and the ready oxidisability of the complexes led to the hypothesis of the η^2-coordination of the trifluoroacetate group in complexes of the type $H_2IrL_2(O_2CCF_3)$ (L = PAr_3)[46] and $[Rh(PPh_3)_2(O_2CCF_3)]_2$.[47] The electrical conductivity found for the complex $Ir(NO)(O_2CCF_3)_2(PPh_3)_2$ permitted the conclusion that it is partly ionised in polar solvents, which confirmed the lability of the M–$OCOCF_3$ bond. Its treatment with sodium tetraphenylborate leads to the complex $[Ir(O_2CCF_3)(NO) \cdot (PPh_3)_2]^+BPh_4^-$ with an anomalously low ν_{OCO}^{as} frequency at 1572 cm^{-1}, which may indicate a bidentate cyclic coordination of the CF_3COO group in this compound.[34,42]

Since TFA is a strong acid, its conjugate base CF_3COO^- is relatively weak and the M–$OCOCF_3$ bond is labile, which, together with the thermal stability of the complexes and the ability of the trifluoroacetate anion to behave as a η^1- and η^2-ligand as well as the chemical resistance of the trifluoroacetate anion to oxidation, makes it attractive to employ TFA in catalytic metal complex systems. The introduction of CF_3COO^- groups into the coordination environment of the central metal atom enhances the electrophilic properties of the complexes, which as a rule ensures the possibility of the occurrence of the reaction at a lower temperature.

III. Reactions of hydrocarbons with participation of electrophilic metal complexes in trifluoroacetic acid

1. Activation of the C–H bond by metal complexes

Analysis of the literature data on the reactions of alkanes in solutions of metal complexes shows that a whole series of possible mechanisms of the primary interaction between the components exist.[2,3] The complexity of the problem of the activation of alkanes arises from their chemical inertness. In most of the known reactions leading to the formation of stable molecular products, one of the strong covalent C–H or C–C bonds in alkanes must be ultimately broken. In this respect, the problem of the activation of a C–H σ-bond of a paraffin is similar to that of the activation of the hydrogen molecule.[2,48]

Alkanes are very weak electron donors and poor electron acceptors.[2] However, the occurrence of intramolecular interactions between a nonactivated C–H sp^3-bond of the ligand and the transition metal atom surrounded by ligands has been noted in a series of structural studies.[49,50] The term 'agostic' bond has been proposed for this interaction;[51] data on complexes with such bonds have been summarised in two communications.[52,53] It has been shown that the electron deficiency of the metal is a necessary but not sufficient condition for the formation of the agostic bond. The metal must also possess fairly strong acid properties. Thus the replacement of π-acceptor ligands in the complex by π-donor ligands weakens the agostic bond.[54]

The low reactivity of saturated hydrocarbons is associated with the absence of low-lying unoccupied orbitals in the latter (the first band in the electronic absorption spectra of alkanes is located in the region above 10 eV). The transition state in reactions of such compounds frequently involves the excitation of electrons to antibonding orbitals. The reactivity of alkanes should accordingly be highest relative to species having low-lying unoccupied orbitals, i.e. electrophiles. The reactions of methane in superacids[55] and of its homologues in organic superacids[15] are well known. A high oxidation state of the central transition metal ion also favours the formation of its complexes with alkanes, which follows, in particular, from the similarity between these reactions and those of alkanes in superacids, which proceed with formation of carbenium ions.[55]

$$RH + H^+ \rightleftharpoons RH_2^+$$

Analysis[56] carried out for different types of interaction of C–H bonds with transition metals permits the following conclusions:

1. One-electron transfer reactions on treatment with oxidants which are stable in aqueous solutions are thermodynamically impossible for alkanes (the equilibrium oxidation–reduction potentials of the RH^+/RH pairs are 3.4–4.1 V).

$$L_nM + RH \longrightarrow L_n\bar{M} + RH^+$$

On the other hand, strong oxidants can abstract an electron from aromatic compounds (the corresponding oxidation–reduction potentials are in the range 1.6–2.0 V).

2. The mechanism of the reactions of alkanes with metal complexes involving the formation of free radicals with the simultaneous abstraction and solvation of a proton can be regarded as probable in the case of strong oxidants such as Co(III), Cr(VI), and Mn(VII), particularly in solutions of strong acids in which the oxidation-reduction potential of the $M^{(n+1)+}/M^{n+}$ pairs is a maximum.

$$L_nM + RH \longrightarrow L_n\bar{M} + \dot{R} + H^+$$

3. The formation of a M–R bond, coupled with the liberation and formation of H^+, diminishes the requirements as regards the strength of the oxidant. For the electrophilic substitution reaction

$$L_nM + RH \longrightarrow L + L_{n-1}\bar{M}R + H^+,$$

the energy expenditure on the creation of a coordination vacancy (E) is given by [56]

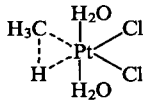
$$E = E(M-L) - Q_s(L) - Q_s(ML_{n-1}) + Q_s(ML_n),$$

where Q_s are the heats of formation of the system components.

Thus substitution is promoted by a low bond energy $E(M-L)$ and high enthalpy of solvation of the ligand $Q_s(L)$.

The substitution of H^+ by a metal ion M^+ as a result of the interaction of hydrocarbons with metal complexes is characteristic of aromatic compounds (mercuration and thallation reactions). For a high strength of the M–C bond, such a step becomes possible also for alkanes, but it differs from classical electrophilic substitution. For example, the interaction of platinum(II) complexes with alkanes [1] apparently begins with the oxidative addition of a C–H bond, which leads to the formation of an alkylplatinum(IV) hydride complex and terminates with the synchronous formation of a Pt(II)–C bond and the elimination of a proton. The proton may be bound by a water molecule, which is a stronger base than the Pt centre. [2,56]

The results of a quantum-chemical study [57] of the model reaction of methane with the complex *trans*-$PtCl_2(H_2O)_2$ have shown that, in the initial stage of the interaction before the attainment of the transition state, the C–H bond is polarised with a significant intensification of the acidity of the hydrogen atom without change of the charge on the platinum.



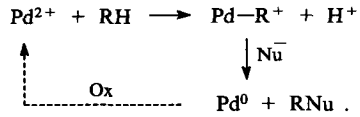
In the presence of a base stronger than the platinum(II) complex, the transfer of H^+ to a molecule of the base is easier than the continuation of the oxidative addition process after the loosening and polarisation of the C–H bond [as a result of the initial stage of the interaction of CH_4 with Pt(II)]. The binding of the leaving group to the base is the driving force of the electrophilic substitution reaction. [48] The addition of methane with participation of zirconium complexes, [58] for example $(RNH)_2Zr$ = NR, where R = $SiBu^t_3$, may serve as an example of such interaction.

The study of the cyclometallation reactions has shown that cyclopalladation is predominantly electrophilic in character, whilst the interaction of a C–H bond of a coordinated ligand with platinum(II) is more likely to proceed via an oxidative addition mechanism. [59] The type of mechanism depends on the nature of the metal and the substrate or, which appears more likely, the balance between the steric and electronic factors determines the final product in each case. For example, the rate of the cyclometallation reaction increases in the sequence Cl < Br < I for PdX_2L_2 (L = hindered phosphine; X = Cl, Br, I), whilst the reverse sequence obtains for phosphite complexes. [59]

2. Reactions of hydrocarbons with participation of palladium complexes

Palladium occupies a special place in the series of oxidants. It is a good electrophile, [60] a typical two-electron oxidant, and can be reoxidised by fairly mild oxidants, which permits its use in catalysis. [61–63]

Scheme 1



a. Palladium(II) trifluoroacetate

Palladium(II) trifluoroacetate and acetate are trimeric in the crystalline state, but in benzene at 37 °C the trifluoroacetate is monomeric, in contrast to the acetate. [32,35,39] According to X-ray photoelectron studies, the influence of the ligands in palladium(II) compounds affects strongly the position of the Pd($3d_{5/2}$) level, the range of variation of the binding energy E_b amounting to 2 eV depending on the ligands. The binding energies of the internal electrons of the palladium atoms in complexes with ligands having pronounced π-acceptor properties are especially high (Table 1); the closest approximation to E_b [Pd($3d_{5/2}$)] for palladium(IV) is observed in the case of $Pd(O_2CCF_3)_2$, which agrees with the pronounced electron-accepting properties of palladium in this compound.

Table 1. The Pd($3d_{5/2}$) binding energies in palladium complexes.

Complex	E/eV	Ref.
Pd (metal)	335.8	64
$PdCl_2$	338.0	65
K_2PdCl_4	338.4	65
$Pd(O_2CCH_3)_2$	338.8	64
$Pd(CH_3CN)_4(PF_6)_2$	339.5	66
$Pd(CN)_2$	339.6	65
$Pd(O_2CCF_3)_2$	339.7	67
K_2PdCl_6	340.3	65

b. Alkanes and cycloalkanes

Palladium differs from platinum by the lower stability of the d^6 state of palladium(IV) and the smaller strength of the Pd–C bond. Oxidative addition via the C–H bonds of alkanes is therefore less probable for palladium(II) complexes than for platinum(II) complexes. On the other hand, it has been found that electrophilic substitution reactions at a carbon atom with participation of the palladium(II) centre proceed extremely effectively. The absorption of alkanes and benzenes, accompanied by the formation of metallic palladium, was observed in 1973–1974 in the $PdSO_4$–H_2SO_4 and $Pd(O_2CCF_3)_2$–anhydrous CF_3COOH systems. [68,69]

Hydrocarbons (hexane, cyclohexane, benzene) reduced $Pd(O_2CCH_3)_2$ or $Pd(O_2CCF_3)_2$ in CF_3COOH at 92 °C. [69] For the ratio $Pd(O_2CCF_3)_2 : CF_3COOH$ = 1 : 10, palladium trifluoroacetate forms a stable homogeneous solution and dehydrogenates cyclohexane in accordance with the stoichiometric equation

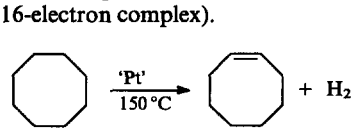
$$3\,Pd(O_2CCF_3)_2 + C_6H_{12} \longrightarrow 3\,Pd^0 + C_6H_6 + 6\,CF_3COOH .$$

Together with benzene, the products of its further reaction—biphenyl and phenyl trifluoroacetate—were detected. The absence of an induction period and autoacceleration as well as direct control experiments ruled out the possibility that the reaction takes place on the surface of precipitated metallic palladium. The reactivity of the hydrocarbons in the reaction with palladium trifluoroacetate decreases in the sequence benzene > cyclohexane > hexane.

Cyclohexane and methylcyclohexane are also dehydrogenated in the presence of the so called platinum(III) complexes [mixed-valence platinum(II) and platinum(IV) dimers] to benzene and toluene respectively.[70] It is noteworthy that palladium and platinum acetates are inert in CH_3COOH to hydrocarbons. The dehydrogenation of cycloalkanes apparently proceeds stepwise like the dehydrogenation of hydrocarbons in the presence of palladium(II) in solution in H_2SO_4.[71] This is confirmed by the detection of small amounts of cyclohexene in the dehydrogenation of cyclohexene with participation of platinum(III) complexes and by the rapid disproportionation of cyclohexene[72] to cyclohexane and benzene in the presence of palladium trifluoroacetate.

In contrast to platinum complexes, deuterium exchange is not observed in saturated hydrocarbons in solution in CF_3COOD following the addition of $Pd(O_2CCF_3)_2$, which is caused by the lower stability of palladium alkyls (see Scheme 1) compared with platinum alkyls. Indeed the reactions of the organomercury compounds RHgBr (R = CH_3, C_2H_5) with $Pd(O_2CCF_3)_2$ in CF_3COOD lead to ethane in the first case and to ethylene in the second, neither compound containing deuterium.[68] The decrease in the multiple exchange parameter M (the average number of deuterium atoms incorporated in the product molecule during one step of the interaction) to 1.34 in the H–D exchange in cyclohexane in the presence of $Pt(O_2CCF_3)_2$ in CF_3COOD compared with platinum(II) chloride complexes (M = 1.8) also indicates a decrease in the stability of the Pt–C bond with enhancement of the electron-accepting capacity of the ligand.[73] It is noteworthy that, on alkylation of $Pt(O_2CCF_3)_2$ with ethylmercury bromide in the gas phase, a significant increase in the fraction of ethylene, formed as a result of the β-elimination of hydrogen (ethylene : ethane = 9 : 1), is observed compared with the alkylation of $PtCl_2(H_2O)_2$ (ethylene : ethane = 1 : 3).

It has been shown[74,75] that the replacement of a chloride ion in platinum(II) complexes by the strong π-acceptor ligand $SnCl_3^-$ makes it possible to carry out reactions in organic media and favours dehydrogenation and hydrogen transfer for cyclohexene and cyclohexa-1,3-diene but not cyclohexane. Metallic platinum separated in the course of the reaction, but, as in the case of the H–D exchange in the presence of $PtCl_4^{2-}$,[1] it did not exhibit a catalytic effect. It was later found that a neutral complex of the pentacoordinated platinum(II) with π-acceptor ligands, namely $Pt(SnCl_3)_2[P(OR)_3]_3$ (R = CH_3, C_2H_5), which possesses electrophilic properties, dehydrogenates cycloalkanes with liberation of molecular hydrogen.[76] The authors believe that the active species is the coordinatively unsaturated d^8-ML_4 (a 16-electron complex).



Thus the π-acceptor properties of the ligands are decisive in preventing the reduction of Pt(II) to Pt(0) during the reaction. The strong σ-donor properties of $SnCl_3^-$, which should promote the transition Pt(II) → Pt(0), are evidently of secondary importance. This is the first example of a reaction of this type for platinum complexes. It had been shown earlier that linear cyclic alkanes are dehydrogenated both thermally and photochemically to the corresponding alkenes in the presence of the complex $IrH_2(OCOCF_3)[P(FC_6H_4)_3]_2$.[46] *tert*-Butylethylene is used as a hydrogen acceptor in the thermal dehydrogenation reaction, but in the photochemical process it is not required. The activity of the above iridium complex is determined by the ability of the CF_3COO^- group to behave both as a η^1- and η^2-ligand, which ensures the occurrence of β-elimination in the intermediate alkyliridium hydride complex $Ir(H)(R)(\eta^2\text{-}OCOCF_3)(PR_3)_2$. The iridium complex with the acetate anion is inactive in the dehydrogenation of alkanes. The thermocatalytic formation of molecular hydrogen and cyclooctene from cyclooctane in the presence of rhodium complexes has also been described.[77]

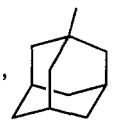
A negative test with metallic mercury showed that the colloidal metal, formed apparently at temperatures in the range 150–180 °C, does not participate in the reaction of the substrate.

As already noted,[72] rapid disproportionation of cyclic olefins is observed in the presence of palladium trifluoroacetate at room temperature. When maleic acid is introduced as a hydrogen acceptor, they are dehydrogenated to substituted benzenes, the rate of formation of the aromatic compound in the presence of $Pd(O_2CCF_3)_2$ being appreciably higher than the rate of reaction with participation of $Pd(O_2CCH_3)_2$.

Later studies extended the range of hydrocarbons which can react with palladium(II) in TFA. The reaction of adamantane or methane with palladium acetate in TFA at 80 °C affords adamantyl trifluoroacetate and methyl trifluoroacetate respectively in 60% yield.

$$RH + Pd(O_2CCH_3)_2 \xrightarrow{CF_3COOH} CF_3CO_2R + Pd^0 + H^+;$$

R = CH_3,



.

The significant role of the quality of palladium acetate, especially in the oxidation of methane, was indicated. When the reaction was carried out with $Pd(O_2CCD_3)_2$, deuterium was not detected in the reaction product, which indicates, in the authors' view, the stability of the acetate group under the reaction conditions. Oxygen does not affect the reaction, which demonstrates the absence of radical stages. The test with metallic mercury for the heterogeneity of the reaction gave a negative result.[79] Since it has been stated in a number of investigations[80,81] that the high yields of the methane oxidation products are not reproducible in the presence of $Pd(O_2CCH_3)_2$ in TFA, the source of the differences is probably the acetate ion present in the study of Gretz and coworkers.[78,79]

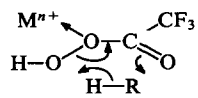
Pronounced electrophilic properties are retained even in the palladium(II) centre surrounded by phosphine ligands when aromatic C–H bonds are attacked. The alkylation of aromatic compounds by alkylpalladium complexes, in particular $(PhCH_2)ClPd(PPh_3)_2$, has been investigated. Experiments using a 1 : 1 C_6H_6–$CH_3OC_6H_5$ mixture showed[82] that the rate of alkylation of anisole is three times higher than that of benzene, which confirms the electrophilic character of the RPd^+ species.

Platinum and rhodium trifluoroacetates also interact with ethane at 80–150 °C and a pressure of 10–15 MPa with formation of methyl trifluoroacetate (0.5%–5.0%), the metal black, CO_2, and fluoroform.[81] The presence of CF_3H among the products indicates the instability of TFA under the reaction conditions and the possible involvement of the trifluoromethyl radical or cation in the C–H bond dissociation processes in methane. The presence of the acetate ion, which is even less stable in relation to decarboxylation, may lead, with a high degree of probability, to the formation of analogous intermediates in systems based on palladium acetate.[78,79] These intermediates can be the cause of the high yield of methyl trifluoroacetate, which is not reproduced in systems based on $Pd(O_2CCF_3)_2$.

Hydrogen peroxide has been used as the oxidant in the reactions of methane with $Pd(O_2CR)_2$ (R = CH_3, C_2H_5) in trifluoroacetic anhydride [90 °C, $p(CH_4)$ = 9 MPa].[83] It has been shown that the yield of $CF_3CO_2CH_3$ passes through a maximum as a function of time. In view of the hydrolysis of $CF_3CO_2CH_3$, the methane oxidation reaction can be represented by the equation

$$CH_4 + H_2O_2 \xrightarrow[(CF_3CO)_2O]{Pd(O_2CR)_2,\ 90\,^\circ C} CH_3OH + H_2O\,.$$

Excess of trifluoroacetic anhydride (TFAN) binds the water evolved during the reaction, preventing hydrolysis of the esters. In this system, palladium(II) can either oxidise ethane, being converted into a zerovalent palladium compound which is then oxidised by CF_3COOOH completing the catalytic cycle, or it can provide electrophilic cooperation in the reaction of the CF_3COOOH molecule with CH_4 by coordination to the oxygen of the peroxy-group in a transition state of the type [84]



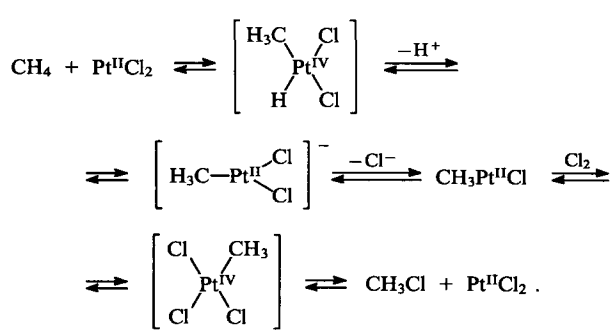
It has been stated that, under the reaction conditions, the acetate group is oxidised with formation of methyl trifluoroacetate. Similar data on the oxidation of CH_3COO^- in the presence of MnO_4^- with formation of $CF_3CO_2CH_3$ have been published. [81]

It has been observed that one of the methane oxidation products is methyl trifluoroacetate in the $V^V-H_2O_2-RCOOH$ system, where R is CH_3 or CF_3, under mild conditions [$p(CH_4)$ = 3–3.5 MPa, 20 °C]. [85]

Irradiation with light of a solution of adamantane and $Pd(O_2CCF_3)_2$ or $Cu(O_2CCF_3)_2$ in CH_3CN leads to the oxidation of the hydrocarbon mainly at the tertiary C–H bond. [86] Alkyl(aryl) trifluoroacetates are formed on irradiation with light of solutions of alkanes(arenes) in TFA in the presence of vanadate ions. [87]

In the presence of a deposited highly electrophilic rhodium(III) complex, methane is chlorinated with formation mainly of methyl chloride. [88] The authors of the above study postulated that the coordinatively unsaturated rhodium(III) attacks a C–H bond of the hydrocarbon. A proton then migrates to the ligand in the coordination sphere of rhodium. A more detailed study of the possible formation in this system of the catalytically active $[SiO]-Rh(\eta^3-C_3H_5)(H)$ showed [89] that the activation of the C–H bond is apparently a result of the classical mechanism of the dissociation of a C–H bond in an alkane on the surface of a metal and is not caused by the electrophilic cleavage in the presence of rhodium(III).

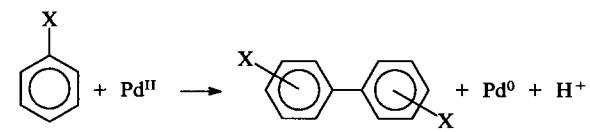
A platinum(II)-modified heterogeneous catalyst for the oxidative chlorination of methane, namely $CuCl_2 + Pt^{II}/Al_2O_3$, has been obtained. [90] It is more active as a result of the appearance of a new reaction pathway involving the formation of methylplatinum(II) complexes. Methylplatinum(II) is subsequently oxidised by molecular chlorine with liberation of CH_3Cl. On the basis of earlier data, [2,90] Olah [55] demonstrated that the heterogeneous-catalytic technology for the synthesis of methanol and olefins via methyl halides is promising.



A new selective low-temperature (200–400 °C) catalyst, namely $[PdCl_2-H_9(PV_6Mo_6O_{40})]/SiO_2$, for the oxidative chlorination of methane with formation of methyl chloride has been discovered. [91] The absence of polychloromethanes and molecular chlorine from the reaction products may indicate the electrophilic properties of the system, which agrees with the behaviour of palladium in other reactions. It has been noted [92,93] that the selectivity of the oxidation of hydrocarbons in the presence of the heterogeneous analogue $(PdSO_4-H_2SO_4)/SiO_2$ (220 °C) is lower than for the homogeneous system. [3] One of the functions of H_2SO_4 as a strong Brønsted acid is to increase the oxidising capacity of palladium(II) and to enhance its electrophilicity.

c. Aromatic compounds

The oxidative coupling of arenes on treatment with palladium(II) compounds was discovered in 1965. [94] These reactions take place in organic and, more rarely, in aqueous solutions at a temperature not exceeding 120 °C.



X = H, Alk, Hal, Ar, OR, O_2CR, OH, etc.

In the general case, a mixture of all possible isomers of biaryls is formed, their ratios being determined by the nature of the substituent X.

When $Pd(O_2CCH_3)_2$ is used instead of the complex $PdCl_2-CH_3COONa$, acetoxylation in the ring and, in the case of methylbenzenes, in the alkyl group takes place together with oxidative dimerisation. Perchloric acid inhibits the acetoxylation reaction, while the introduction of sodium acetate increases the yield of the product acetoxylated in the methyl group. [61,62,95,96]

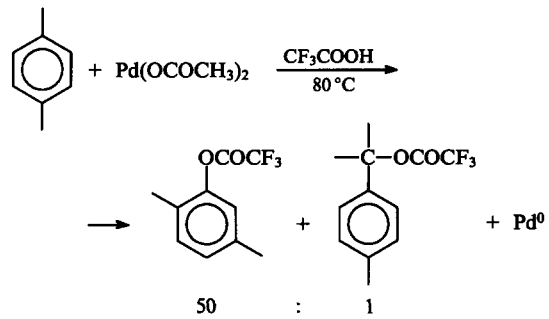
The reactions of palladium with aromatic compounds in TFA occupy a special place. Benzene and its derivatives containing electron-accepting groups reduce palladium trifluoroacetate mainly with formation of oxidative dimerisation products [67] and also of small amounts of trifluoroacetoxylated derivatives under conditions where palladium acetate is inert to aromatic compounds. The preferential formation of oxidative coupling products has been attributed to the decrease in the basicity of the ligand on passing from acetate to trifluoroacetate.

Organopalladium compounds have been isolated in the reaction of benzene and naphthalene with palladium trifluoroacetate in TFA. On the basis of chemical reactions and IR and NMR spectra, Azzoumanidis and Rauch [97] considered these compounds as π-arene complexes in which there is a Pd–C bond. Palladium(II) acetate reacts with benzene in the presence of dialkyl sulfides at 70 °C with formation of a new diphenyltripalladium(II) complex, $(R^1SR^2)PhPd(\mu\text{-}CH_3CO_2)_2Pd(\mu\text{-}CH_3CO_2)_2.PdPh(R^1SR^2)$, where $R^1 = R^2 = Bu^t$, Bu^i, Pr^i, Et, or CH_2Bu^t. [98] The study of these complexes demonstrated the presence in their structures of two phenyl groups and four bridging acetate groups.

As already mentioned above, [67] benzene and mono-, di-, and poly-substituted benzenes reduce palladium(II) in TFA. Benzene, *m*-xylene, and 1,2,3-trimethylbenzene then form mainly biaryls. The reactions of toluene and *p*-xylene involve the appearance of a new pathway, which leads to diarylmethanes. It becomes the main pathway for aromatic compounds with a low ionisation potential. [99]

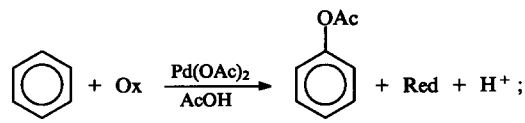
Studies on the interaction of palladium trifluoroacetate with benzene, *p*-dimethoxybenzene, *p*-xylene, and toluene confirmed the electrophilic nature of the process, [79] because the C–H benzyl bonds were hardly attacked by palladium, as in Henry's study. [100] The increase in the rates of oxidation of benzenes containing electron-donating groups in the sequence *p*-dimethoxybenzene (1), *p*-xylene (0.1), toluene (0.02), benzene (0) (the rates are indicated in brackets) is consistent with the electrophilic attack by palladium on the C–H bond, while the primary kinetic isotope effect (k_H/k_D) for the oxidation of toluene and toluene-d_8 is 5.0, which is characteristic of analogous electrophilic systems. [61,62]

It is noteworthy that, in their analysis of the reactivity of aromatic compounds, Sen et al. [79] take into account only the acetoxylation reaction and ignore the oxidative coupling reaction.



d. The effect of the oxidant

The reactions of aromatic compounds with participation of palladium can be carried out under catalytic conditions using fairly mild oxidants. However, the oxidant not only participates in the reoxidation of palladium but is also capable of altering the mode of reaction. [100] In the absence of the oxidant, only oxidative coupling is observed, while in its presence the acetoxylation reaction occurs.



Ox = Cr(IV), $Pb(OAc)_4$, $NaClO_3$, $KMnO_4$, $NaNO_3$, $NaNO_2$.

In addition, there is a possibility of substitution in the aromatic ring by an external nucleophile Nu = N_3^-, Cl^-, NO_2^-, Br^-, CN^-, or SCN^-. Eberson and Jönsson [101] investigated in detail the ring acetoxylation reaction. They showed that the use of a bipyridylpalladium complex and $K_2S_2O_8$ as the oxidant makes it possible to carry out the acetoxylation reaction with formation of a smaller proportion of the *m*-isomer. [101] Potassium persulfate has also been used to oxidise the palladium formed as a result of the interaction of naphthalene with $Pd(O_2CCH_3)_2$ in solution in TFA. [78] The use of oxygen as the oxidant for zerovalent palladium [102] in reactions of aromatic compounds with palladium(II) leads, in contrast to other oxidants, to the formation of oxidative coupling products. [100] Biaryls are formed in high yields in the presence of oxygen also in systems based on palladium salts and heteropolyacids. [103] The oxidation of toluene by oxygen in the $Pd(OAc)_2-Sn(OAc)_2-KOAc-AcOH$ system takes place with formation of benzyl acetate, which indicates the influence of the components of the system on the nature of the processes occurring in it. [104] In particular, the oxidation of divalent tin salts involves the formation of active intermediates (for example, the OH radical), [105] which can in fact be responsible for the attack on the methyl group in the system mentioned above.

Attempts have been made to dehydrogenate cyclohexane with palladium trifluoroacetate in TFA under palladium reoxidation conditions. It was found that TFA attacks oxidants such as chromium(VI) and manganese(VII), enhancing their electron-accepting properties such that they are able to oxidise hydrocarbons rapidly without the participation of palladium. [70,81] However, aromatic compounds are formed only in the presence of palladium(II). Analogous results have been obtained by Sen and coworkers [106] for a wide range of cyclohexane derivatives.

e. The mechanism of the interaction of hydrocarbons with palladium

The mechanism adopted for the oxidation of arenes by palladium(II) includes the formation of an organopalladium intermediate and its reactions without the participation of free radicals. [61,62]

$$ArH + Pd^{2+} \longrightarrow ArPd^+ + H^+$$
$$2\,ArPd^+ \longrightarrow Ar_2Pd + Pd^{2+}$$
$$Ar_2Pd \longrightarrow Ar_2 + Pd^0$$

It has been shown by Kozhevnikov et al. [107] in a study of the oxidation of *o*- and *p*-xylenes by palladium(II) trifluoroacetate in TFA that the formation of diarylmethanes in a strongly acid medium can be explained by one-electron transfer with participation of aromatic radical-cations as intermediates, similar to the oxidation by cobalt(III) and lead(IV) salts. [17] The mechanism of the oxidation of methylbenzenes by palladium(II) (palladation or electron transfer) depends on the type of arene and the acidity of the medium.

$$Pd^{II} + ArH \longrightarrow (\pi\text{-}ArH)Pd^{II} \longrightarrow ArPd^{II} + H^+$$
$$(\pi\text{-}ArH)Pd^{II} \longrightarrow ArH^{+\cdot} + Pd^{I}$$

In relation to the reactions of toluene, palladation has been compared [108] with other aromatic substitution reactions in terms of the ratio of Brown's selectivities $\lg f_n = a \lg (f_n/f_m)$ (for toluene, $a = 1.31$), which characterises the relation between the substrate

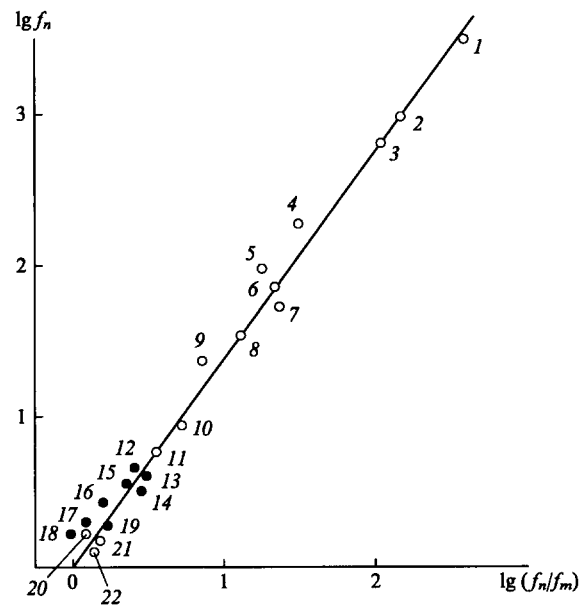


Figure 1. The ratios of selectivities for substitution in the toluene ring. [108] Filled circles — reactions with palladium(II). Bromination: (*1*) Br_2, 85% AcOH, 25 °C; chlorination: (*2*) Cl_2, AcOH, 25 °C; benzoylation: (*3*) PhCOCl in $PhNO_2$, 25 °C; thallation: (*4*) $Tl(O_2CCF_3)_3$, CF_3COOH, 10 °C; (*5*) 73 °C; nitration: (*6*) HNO_3, 90% AcOH, 45 °C; thallation: (*7*) $Tl(OAc)_3 + H_2SO_4$, AcOH, 70 °C; mercuration: (*8*) $Hg(OAc)_2 + HClO_4$, AcOH, 50 °C; (*9*) $Hg(OAc)_2$, AcOH, 50 °C; sulfonation: (*10*) $MeSO_2Cl + AlCl_3$, 100 °C; isopropylation: (*11*) *iso*-$C_3H_7Br + Ga_2Br_2$, 25 °C; palladation: (*12*) $Pd(OAc)_2 + H_2SO_4$, AcOH, 95 °C; (*13*) $Pd(OAc)_2 + HClO_4$, AcOH, 55 °C; (*14*) 95 °C; (*15*) $PdCl_2 +$ NaOAc, AcOH, 90 °C; (*16*) $Pd(OAc)_2 + CF_3COOH$, AcOH, 95 °C; (*17*) $Pd(OAc)_2$ + NaOAc, AcOH, 95 °C; (*18*) $Pd(OAc)_2$ in AcOH, 95 °C; catalytic coupling: (*19*) $Pd(OAc)_2$ in ArH, $p(O_2)$ = 2.5 MPa, 150 °C; radical arylation: (*20*) attacking radical *p*-$NO_2C_6H_4$, 20 °C; (*21*) *p*-$MeC_6H_4^{\cdot}$; (*22*) $\dot{P}h$.

(f_n) and positional (f_n/f_m) selectivities (the positional selectivity characterises the selectivity of the attack on different positions in the ring) of the substitution in the ArH ring. Fig. 1 shows that palladation is the least selective reaction in the series of electrophilic substitution processes, its selectivity approaching that of radical substitution, which is similar to the statistical selectivity with respect to the *meta*- and *para*-isomers.

Table 2 presents the electron affinities and electron excitation energies for a series of electrophiles—transition metals and traditional Lewis acids.[60] Evidently the electron affinity of palladium(II) is comparable to those of zinc(II) and mercury(II). However, palladium(II) has a much lower excitation energy. This leads to a strong donor–acceptor interaction with alkenes and aromatic compounds in the case of palladium (palladium is a soft acid in terms of Pearson's theory of hard and soft acids and bases), which results in the compensation of the influence of the polar (electronic) effects of the substituents in the ArH ring on the reaction centre. A similar result was obtained in a study of the H–D exchange and the oxidation of substituted benzenes in the presence of 'soft' acids—platinum(II) complexes.[109] With increase in the 'hardness' of the ligand environment of palladium(II) (transition from CH_3COO^- to the electron-accepting CF_3COO^- and ClO_4^-), the effectiveness of the compensation falls as a consequence of the weakening of the dative bond. Both the selectivity of the palladation reaction and its rate increase under these conditions. The electrophilic character of the metallation of arenes increases in the sequence Pd(II) < Hg(II) < Tl(III) and the values of ρ are –2.2,[110] –5.3,[111] and –7.5[108] respectively.

Table 2. The excitation energies [$nd^x \rightarrow nd^{x-1}(n+1)p^1$] and electron affinities for a series of metal ions.

Ion	Excitation energy/eV	Electron affinity/eV
Rh(I)	1.6[a]	7.31
Ir(I)	2.4[a]	7.95
Pt(II)	3.05[a]	18.56
Pd(II)	3.39[a]	19.42
Cu(I)	8.25	7.72
Ag(I)	9.94	7.59
Zn(II)	17.1	17.96
Cd(II)	16.6	16.90
Hg(II)	12.8	18.75
Tl(III)	18.3	29.80

[a] The values for Rh^0, Ir^0, Pd^I and Pt^I are presented.

By analogy with the existence of a common intermediate in the H–D exchange and oxidative chlorination of alkanes in the presence of platinum(II) and platinum(IV) complexes, which was postulated and demonstrated by kinetic methods,[2,112,113] in the case of palladation reactions there should also be a common intermediate, which affords the oxidative coupling products in the absence of an added oxidant and ring acetoxylation products in its presence. The primary isotope effect and the dependence of the rate of reaction on the concentration of the acid oxidant have been interpreted within the framework of ideas postulating that arylpalladium(II) and arylpalladium(IV) are intermediates leading to biaryls and aryl acetates respectively.[19,114]

$$Ph_2Pd^{II} \xleftarrow{C_6H_6} PhPd^{II}(OAc) \xrightarrow{Ox} PhPd^{IV}(OAc)_3$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$Pd^0 + Ph_2 \qquad\qquad PhOAc + Pd^{II}(OAc)_2 .$$

3. Carboxylation and oxidation of hydrocarbons with participation of palladium(II)

The formation of reactive organopalladium compounds in the reaction of hydrocarbons with palladium(II) made it possible to achieve the acetoxylation and oxidative coupling of arenes, the arylation of olefins, and also the direct oxidation and carboxylation of aromatic compounds and alkanes.

The stoichiometric carboxylation of arenes with carbon monoxide in the presence of palladium acetate has been carried out.[115] It was found that the reactivity of monosubstituted benzenes diminishes in accordance with the electrophilic character of the reaction in the following series of substituents: $OCH_3 > CH_3 > H > Cl$. The achievement of a single-stage synthesis of aromatic acid anhydrides from compounds such as benzene, toluene, anisole, chlorobenzene, thiophene, and furan, which are carbonylated in the β-position, has been reported.[116] A significant difference between the reaction conditions and those described by Fujiwara et al.[115] is the presence of 1,2-dibromoethane, the role of which is believed by the authors[116] to be the reoxidation of the metallic palladium formed in the reaction. Other polyhalo-compounds diminished the yield of the anhydrides.

$$ArH \xrightarrow[p(CO) = 1.5\ MPa]{Pd^{II}} (ArCO)_2O .$$

In the presence of *tert*-butyl hydroperoxide, the synthesis of aromatic acids with participation of palladium(II) in solution in acetic acid, which permits the use of a low carbon monoxide pressure, becomes catalytic.[117,118]

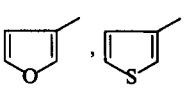
$$ArH \xrightarrow[Ox]{Cat} ArCOOH ;$$

Cat = $Pd(OAc)_2$;
Ox = Bu^nOOH, $CH_2{=}CHCl$, AcOH; $p(CO)$ = 0.1 MPa.

It is of interest to note that certain oxidants—H_2O_2, *m*-ClC_6H_4COOOH, $O{=}C_6H_4{=}O$, $CuCl_2$, $Pb(OAc)_4$, $FeCl_3$, and $K_2S_2O_8$—lower the yield of the oxidative carbonylation products.

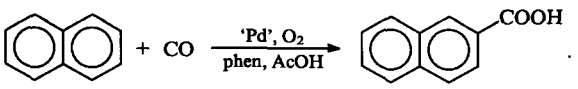
The insertion of CO_2 in the Pd–C bond of an organopalladium compound leads to the formation of acids, but the reaction selectivity is low,[119] the reactivity of CO_2 amounting to approximately 0.01 of the reactivity of CO. The joint employment of palladium(II) and Bu^tOOH increases the yield of aromatic acids in this case too.

$$ArH + CO_2 \xrightarrow{Pd(OAc)_2,\ Pd(NO_3)_2} ArCOOH ;$$

Ar = Ph, ClC_6H_4, $CH_3OC_6H_4$,  .

The proportions of the isomers of substituted benzenes are consistent with their proportions obtained on electrophilic substitution in an aromatic compound.

β-Naphthoic acid can be obtained with a selectivity in excess of 80% by the single-stage carboxylation of naphthalene with carbon monoxide in the presence of palladium(II) under mild conditions.[120]

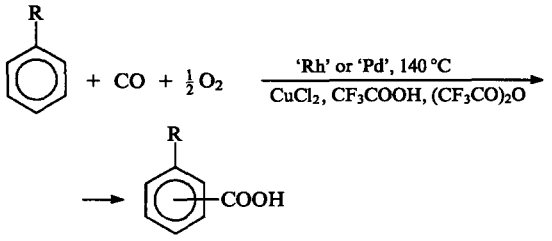


It is significant that the maximum yield of β-naphthoic acid is attained in the simultaneous presence of acetic acid, oxygen, and *o*-phenanthroline (phen), the last compound regulating the reaction selectivity. Palladium on charcoal or palladium black catalyse, like palladium(II) acetate, the carboxylation of naphthalene. The reaction apparently proceeds via a stage involving the formation of a σ-arylpalladium(II) complex via the electrophilic substitution of hydrogen in the aromatic compound in the case of palladium(II) or the oxidative addition of naphthalene in the case of zero-valent palladium. It may be that large palladium clusters, which are in fact the carboxylation catalysts, are formed during the reaction. [121]

The palladium-catalysed carboxylation of aromatic C–H bonds by carbon monoxide takes place with high yields and under mild conditions [p(CO) = 0.1 MPa, 20–50 °C] in TFA in the presence of sodium acetate as the cocatalyst. [122] The yield of the products corresponds to the stoichiometric consumption of palladium, but the reaction can be carried out under catalytic conditions with participation of $NaNO_3$, $Tl(O_2CCF_3)_3$, and $Hg(O_2CCF_3)_2$ like the carboxylation phenylmercury chloride in the presence of palladium(II). [123] The reaction with substituted aromatic compounds, such as anisole and toluene, is a typical electrophilic substitution process. The electrophilic character of the reaction agrees with the positive effect exerted by the addition of strong acids (CF_3COOH). Since in the presence of an oxidant the regioselectivity of the process increases compared with the stoichiometric reaction, thallium(III) and mercury(II) compounds probably not only oxidise the zerovalent palladium formed but also play the role of *ortho*- and *para*-directing agents. The role of sodium acetate is less clear. On the one hand, its presence can weaken the electrophilic properties of palladium (compared with trifluoroacetate) and, on the other, it should stabilise the catalytic system in relation to the reduction of palladium by carbon monoxide. These postulates require the existence of an optimum Pd : NaOAc ratio.

The palladium-catalysed carboxylation of the C–H bonds of thiophene and furan by carbon monoxide proceeds in acetic acid (both compounds are unstable in TFA) with participation of mercury(II) and thallium(III) carboxylates under mild conditions [p(CO) = 0.1 MPa, 20–50 °C]. [124]

The oxidative carbonylation of benzene and its derivatives in the presence of rhodium(III) trifluoroacetate as well as palladium and copper compounds has been investigated. [125]

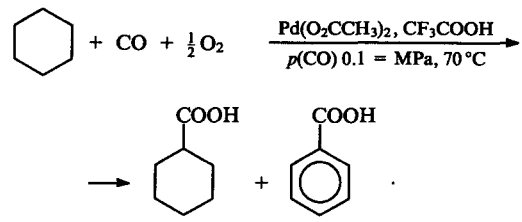


R = H, CH_3, CH_3O, Cl.

We may note that the replacement of rhodium in the form of $Rh(O_2CCF_3)_3$ by $Pd(O_2CCF_3)_2$ leads to a significant increase in the overall yield of toluic acids. It has been shown that, in conformity with the data of Gol'dshleger et al., [126] rhodium(III) trifluoroacetate is an electrophile which directs the carboxy-group predominantly to the *para*-position. We may also note that the system components—the copper(II) compounds CuX_2 (X = CH_3COO, CF_3COO, ClO_4)—themselves effectively catalyse the carboxylation of aromatic compounds.

The Rh^{3+}/nafion catalyst reacts as a strong electrophile: [127] *p*-toluic acid is formed under these conditions with a selectivity of 94%.

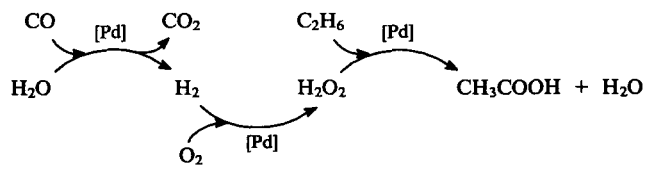
The first study on the carboxylation of cycloalkanes by carbon monoxide without irradiation in the presence of palladium(II) was carried out by Japanese investigators. [128]



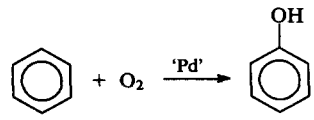
Cyclohexanecarboxylic and benzoic acids are obtained in molar proportions of 1 : 3. Potassium peroxydisulfate proved to be a convenient oxidant in this case also. [129–131] The introduction of methanol and the increase in the reaction time and temperature appreciably increased the yield of cyclohexanecarboxylic acid. [129] The reactivity of the C–H bonds of cycloalkanes diminishes on passing from tertiary to primary bonds. [130] In the case of hexane, the 1-, 2-, and 3-carboxylic acids are obtained in molar proportions of 2 : 29 : 20, [129] which differ appreciably from the photochemical alkane carbonylation reactions in the presence of $RhCl(CO)[P(CH_3)_3]_2$. [9] In this connection, the results obtained in the oxidation and oxidative carbonylation of methane in the presence of potassium persulfate in aqueous solution are of interest. [132] It was shown that the $SO_4^{-\bullet}$ radical-anion, generated from $S_2O_8^{2-}$, abstracts a hydrogen atom from methane and ethane at 105–115 °C with formation of an alkyl radical, which can subsequently effectively interact with carbon monoxide, affording an acyl radical, the latter being converted in the final stages into carboxylic acids, CH_3COOH and C_2H_5COOH respectively, in high yields. It may be that this reaction makes an appreciable contribution to the oxidative carbonylation of cycloalkanes in the presence of the Pd(II)–$K_2S_2O_8$ system [the yield of carboxylic acid relative to the palladium(II) taken for the reaction reached 19 000%]. [131]

The carbonylation of methane by carbon monoxide in solution in TFA in the presence of $K_2S_2O_8$ as the oxidant is possible with participation of copper complexes, which presupposes a reaction mechanism different from the mechanism of the carboxylation of cyclohexane with participation of a σ-organopalladium compound. [133]

A highly effective system for the direct oxidation of lower alkanes by oxygen in aqueous solution has been proposed. [134] Pd/C serves as the catalyst of the low-temperature synthesis of carboxylic acids.



The direct hydroxylation of benzene by molecular oxygen or H_2O with formation of phenol, which proceeds via a stage with C–H bond activation by palladium(II) compounds, has been achieved. The reaction temperature is appreciably higher than the temperature necessary for the carboxylation of aromatic compounds by CO or for the oxidative coupling reaction. The selective synthesis of phenol requires the presence of carbon monoxide, phenanthroline, and oxygen. [135]



The effect of CO on the selectivity of the hydroxylation of aromatic compounds in the presence of palladium(II) is associated with the possibility of the acceptance of one oxygen atom with formation of CO_2, while the other is inserted in the Pd–C bond. A decrease in the concentration of palladium increases the yield of phenol. In the absence of CO, biphenyl is formed in addition to phenol. [136]

4. Reactions of aromatic compounds with participation of platinum(IV)

The interaction of platinum(II) and platinum(IV) complexes with aromatic hydrocarbons has been investigated. [137] The degree of reduction of platinum(IV) in the oxidative coupling of toluene in the $Hg(OAc)_2-H_2PtCl_6-AcOH$ system depends on the acidity of the medium: in a weakly acid medium, the reduction proceeds as far as platinum(II), while in a strongly acid medium it continues to zerovalent platinum with formation in the latter case of two moles of bitolyl per mole of platinum(IV). As in the case of palladium(II), the introduction of perchloric acid apparently increases the electrophilicity of platinum(II), which has been confirmed by data [138] indicating a greater activity of platinum(II) complexes with a low chlorine content — $PtCl(H_2O)_3^+$ and $Pt(H_2O)_4^{2+}$ — in the oxidation of benzene.

Evidence for the formation of relatively stable intermediate acyl and phenyl derivatives of platinum(IV) in the oxidation of methane and benzene in the platinum(II)–platinum(IV) system has been obtained by ^1H and ^{13}C NMR spectroscopy. [12,139]

Further studies demonstrated that σ-arylplatinum(IV) complexes can be obtained in yields up to 95% on heating the aromatic compound ArH with H_2PtCl_6 in CH_3COOH or a $CF_3COOH-H_2O$ mixture. [140,141]

$$ArH + H_2PtCl_6 \xrightarrow[2.\ SiO_2,\ NH_3]{1.\ CF_3COOH-H_2O} NH_4^+\left[(\sigma\text{-}Ar)PtCl_4NH_3\right]^-$$

Naphthalene and *o*-nitrotoluene complexes have been characterised by X-ray diffraction. [140,142] It has been established by the method of competing reactions [143,144] that the relative rates of reaction involving PhX, indicated below in brackets, decrease in the following sequence of X: OH (16), OCH_3 (8.5), CH_3 (3.0), C_2H_5 (2.7), OC_2H_5 (2.0), $CH(CH_3)_2$ (1.9), H (1.0), Ph (0.9), F (0.9), $COCH_3$ (0.1), COOH (0.09), Cl (0.08), NO_2 (0.04). The logarithms of the rates are correlated with Hammett's σ constant and Brown's σ^+ constants (the parameters ρ and ρ^+ are –3.0 and –1.5 respectively). On the basis of the data obtained, a mechanism is proposed for electrophilic substitution in the aromatic ring with participation of platinum(IV) complexes. [145] The behaviour of platinum(IV) in arene metallation reactions resembles that of palladium(II) complexes (ρ ad ρ^+ are –3.0 and –2.2 respectively). [110,144]

It is of interest that the interaction of mesitylene with $PtCl_6^{2-}$ in TFA with formation of (2,4,6,3′,5′-pentamethyl)diphenylmethane in the first stage apparently includes electron transfer from the arene to the platinum(IV) complex. Thus the behaviour of platinum(IV) is similar to that of palladium(II) in TFA. [146]

5. Oxidation of hydrocarbons by cobalt(III), manganese(III), lead(IV), and silver(II) carboxylates

Cobalt(III), manganese(III), and lead(IV) carboxylates are used to oxidise alkyl-substituted aromatic hydrocarbons. [17,19] Whereas cobalt(III) acetate is stable in acetic acid even at a high temperature, manganese(III) acetate decomposes even on slight heating with formation of radicals, which participate in further reactions.

$$\dot{C}H_2COOH \longrightarrow \dot{C}H_3 + CO_2.$$

This mechanism is characteristic of aromatic compounds with an ionisation potential above 8 eV. In the presence of more readily oxidised compounds, $Mn(O_2CCH_3)_3$ reacts via an electron-transfer mechanism with formation of the radical-cation of the aromatic compound. After the addition of a strong acid, this pathway becomes the only one. [147] The introduction of a strong acid such as CF_3COOH plays a decisive role in the interaction of these oxidants with benzene, toluene, and unsaturated hydrocarbons. [148–152] The effect of TFA may be attributed to the formation of a cationic species which renders cobalt(III) a stronger electrophile. [147]

$$Co(O_2CCF_3)_3 \longrightarrow Co(O_2CCF_3)_2^+(CF_3COO)^- \xrightarrow{H^+} \longrightarrow Co(O_2CCF_3)_2^+ + CF_3COOH$$

As a result, the oxidation of alkanes by cobalt(III) acetate in TFA becomes possible at low temperatures. Under an inert atmosphere, the reaction products are esters while in the presence of oxygen ketones are formed. When CCl_3COOH was used as the activator, alkyl chlorides, primarily secondary alkyl chlorides, were obtained under an inert atmosphere. Cobalt(III) trifluoroacetate was quantitatively reduced in TFA by cyclooctane and 2,3-dimethylbutane in 2 and 3 h respectively, but the esters were formed in a low yield. Cyclohexyl trifluoroacetate was obtained in a yield of 35% under similar conditions, which indicates its subsequent transformation under the reaction conditions (for example, the splitting off of TFA and subsequent reactions of cyclohexene). However, benzene was oxidised quantitatively to phenyl acetate with participation of $Co(O_2CCF_3)_3$ at room temperature. [151]

The interaction of manganese(III), iron(III), cobalt(III), copper(II), and lead(IV) trifluoroacetates with methane in solution in TFA at 100–200 °C and a methane pressure of 1–4 MPa has been investigated. The activity of the metal trifluoroacetates diminishes in the sequence Co(III) > Mn(III) > Pb(IV) ≫ Cu(II) > Pd(II); $Fe(O_2CCF_3)_3$ was inactive. The degree of formation of methyl trifluoroacetate reaches 90% in the case of cobalt(III) and takes place in conformity with the following equation: [80,153]

$$CH_4 + 2Co(O_2CCF_3)_3 \longrightarrow \longrightarrow CF_3CO_2CH_3 + 2Co(O_2CCF_3)_2 + CF_3COOH.$$

Further study of this system showed that the addition of oxygen (0.1–0.5 MPa) to methane leads to the catalytic synthesis of $CF_3CO_2CH_3$ from methane. The same yields of methyl trifluoroacetate were attained in the $Co(III)-O_2-CH_4$ and $Co(II)-O_2-CH_4$ systems. [80]

$$CH_4 + \tfrac{1}{2}O_2 + CF_3COOH \xrightarrow{\text{'Co'}} CF_3CO_2CH_3$$

It has been found [154] that ethane and propane also react with $Co(O_2CCF_3)_3$ under similar conditions in solution in TFA with formation of alkyl trifluoroacetates as the main products.

$$C_2H_6 + 2Co(O_2CCF_3)_3 \longrightarrow \longrightarrow CF_3CO_2C_2H_5 + 2Co(O_2CCF_3)_2 + CF_3COOH$$

$$C_3H_8 + 2Co(O_2OCF_3)_3 \longrightarrow \longrightarrow \textit{iso}\text{-}C_3H_7O_2CCF_3 + 2Co(O_2CCF_3)_2 + CF_3COOH$$

As in the case of methane, this interaction is accompanied by the decarboxylation of TFA, catalysed by cobalt salts, with formation of CO_2 and CF_3H. The oxidation of ethane and propane is a less selective process than the oxidation of methane. A reaction mechanism has been proposed. It involves direct electron transfer from the alkane RH molecule to Co(III) with formation of the radical-cation $RH^{+\bullet}$ in the first stage, as in the oxidation of alkanes in the presence of $Co(O_2CCH_3)_3$.

It has been found that bis(bipyridyl)silver(II) peroxydisulfate oxidises aromatic compounds in acetic acid at room temperature. The system becomes catalytic with respect to silver when an excess of potassium persulfate is used. [155]

Adamantane and other cyclic compounds are oxidised with a satisfactory yield to adamantyl and cycloalkyl trifluoroacetates [156] by the silver 'peroxide' $Ag(I)Ag(III)O_2$, which generates an active Ag(III) complex in the TFA–TFAN mixture.

6. Oxidation of hydrocarbons by manganese(VII), chromium(VI), and ruthenium(IV) in acetic acid

The oxidation of alkanes, cycloalkanes, and aromatic compounds by potassium permanganate $KMnO_4$ in aqueous trifluoroacetic acid has been investigated. It was found that the oxidising capacity of manganese(VII) increases with increasing acid concentration. The rate of oxidation of alkanes by manganese(VII) is sensitive to the structural differences in the substrate, in particular to the branching of the chain. A series of specific rates have been observed in terms of the selectivity of the oxidation of primary, secondary, and tertiary C–H bonds: 1, 60, and 2100 respectively. The rate of oxidation increases with increase in chain length; the methylene group is more reactive than the methyl group. After the introduction of electron-accepting substituents in the carbon chain, the rate of reaction falls. The primary isotope effect, determined for $C_6H_{12}-C_6D_{12}$ as 4.3, confirms that the rate-determining stage of the reaction is the cleavage of a C–H bond. It has been suggested [157] that the active species is the permanganyl cation MnO_3^+ in the free form or as the ester $MnO_3(O_2CCF_3)$.

The rate constants and the substrate selectivities for the first stage of the oxidation of RH (C_2-C_8 alkanes, benzene, toluene) by permanganate in TFA–H_2O solutions have been determined from the consumption of the substrate. [158] These data differ significantly from the results of the study of Stewart and Spitzer [157] obtained by a standard method from the consumption of the oxidant. Arguments have been put forward in support of the hypothesis that the reactants in solutions in TFA are MnO_4^-, $HMnO_4$, and $MnO_3(O_2CCF_3)$, the contribution of the last species becoming significant at a TFA concentration in excess of 50 mass%.

In the presence of manganese(VII), toluene in TFA is oxidised to CO_2, but, with increase in the concentration of water, the yield of benzoic acid increases; [159] rapid degradation of the aromatic compound, which follows the electrophilic attack by MnO_3^+, was also noted. [157]

Solutions of $KMnO_4$ in the TFA–TFAN mixture are capable of oxidising selectively methane to the product of its two-electron oxidation—methyl trifluoroacetate. [160–161] Methyl trifluoroacetate and methyl formate are formed in solution in the course of several hours at 60 °C and $p(CH_4)$ = 20 MPa, their overall yield reaching 90% relative to the unused oxidation equivalents of manganese(VII), converted during the reaction into manganese(IV) and manganese(III), in proportions of 3:1, which are inactive with respect to methane and sparingly soluble. Dimethyl formal $(CH_3O)_2CH_2$ is also formed (2%–4%). Fluoroform and carbon dioxide were detected in the reaction products, their amount corresponding to the consumption of ~10% of the oxidation equivalents of manganese(VII) on decarboxylation of TFA. The addition of small amounts of water reduces sharply the yield of the partial oxidation products as a result of the hydrolysis of the esters to methanol, which is relatively rapidly oxidised by potassium permanganate to CO_2. The use of methane enriched in $^{13}CH_4$ affords products containing the corresponding amount of the ^{13}C isotope. Manganese(VII) participates in the primary interaction with a methane molecule in the form of the cation MnO_3^+ or the ester $MnO_3(O_2CCF_3)$, the rate constants for this interaction amounting to 4×10^{-5} litre mol^{-1} s^{-1} at 70 °C and 1.5×10^{-5} litre mol^{-1} s^{-1} at 60 °C, which is higher than the corresponding constant for the $HMnO_4$ species determined in sulfuric acid solutions (10^{-5} litre mol^{-1} s^{-1} at 70 °C) and exceeds by three orders of magnitude the rate constant for the MnO_4^- species determined in neutral aqueous solutions. [160] Thus the rate constant for the reaction of methane with the manganese(VII) species increases sharply with increase in their electrophilicity.

In the presence of a large excess of sodium periodate, capable of oxidising in acid media the final product of the stoichiometric reaction [manganese(IV) and manganese(III) compounds] to permanganate, the process becomes catalytic with respect to the initial manganese both in aqueous acid media (10 cycles) and in TFA (2–3 cycles). [161] A simplified mechanism of the interaction for the TFA solutions is as follows:

$$\tfrac{2}{3}Mn^{VII} + CH_4 \xrightarrow[70\,^\circ C]{CF_3COOH} CF_3CO_2CH_3 + \tfrac{2}{3}Mn^{IV} + H_2O\,.$$

$$\tfrac{2}{3}Mn^{IV} \xrightarrow{NaIO_4} \tfrac{2}{3}Mn^{VII}$$

We may note that, in the absence of permanganate, the periodate exhibits an intrinsic activity in the oxidation of methane, which, however, is 20–30 times lower than the activity of permanganate. This apparently indicates unusual properties of oxo-complexes of metals in the C–H bond activation reaction and the fact that a higher standard two-electron redox potential of the periodate/iodate couple is insufficient for a more effective oxidation of the C–H bond.

A similar set of products [$CF_3CO_2CH_3$, CH_3CO_2H, $(CH_3O)_2CH_2$, CO_2, and CF_3H] was also found in the oxidation of methane in TFA by chromium(VI) compounds. [161]

A solution of potassium dichromate in TFA at room temperature oxidises n-pentane to the trifluoroacetic acid esters of 2-pentanol and 3-pentanol in molar proportions of 2:1 respectively. [162] Apart from these esters, the formation of small amounts of acetic and propionic acid was observed. Kinetic and spectrophotometric study of the reaction showed that the mononuclear chromium(VI) complexes are inactive and that the two-electron oxidation of a C–H bond of the methylene group of the alkane is effected by the dimeric complexes [$Cr^{VI}\cdots Cr^{VI}$]. The role of the second chromium ion in the complex apparently reduces to the enhancement of the electron-accepting properties of the oxo-groups of the first ion, [3] which serve as the active centre for the electrophilic interaction with a C–H bond of the alkane.

Extremely pronounced oxidising properties are characteristic of chromyl trifluoroacetate: in its presence, hydrocarbons reacted at temperatures in the range –20 to 25 °C in solvents without a C–H bond such as CCl_4 and $F_2ClC-CF_2Cl$. [163]

$$RH + CrO_2(OCOCF_3)_2 \longrightarrow$$

$$\longrightarrow \left[CF_3CO_2\overset{HO\quad R}{\overset{\diagdown\ \diagup}{Cr}}O_2CCF_3\right] \longrightarrow ROH\ (RO_2CCF_3)\,.$$

Ruthenium(IV) trifluoroacetate was used for the first time in the study of Lardais et al. [164] for the oxidative coupling reaction. The yield of the products of the oxidative dimerisation of phenylalkylisoquinolines in its presence was higher than in the case where $Tl(OCOCF_3)_3$ had been used.

7. Reactions of olefinic hydrocarbons with transition metal carboxylates

The oxidation, dehydrogenation, oxidative coupling, acetoxylation, and carboxylation reactions of saturated and aromatic hydrocarbons, which take place effectively when acted upon by metal complexes with electron-accepting ligands, were examined above. Reactions such as the oxidation of olefins, conversion into cyclopropane derivatives, and cyclodimerisation of strained hydrocarbons are also sensitive to the electron-accepting properties of the carboxylate ligand. Several examples are presented below.

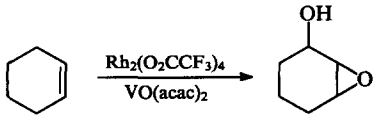
tert-Butyl peroxide complexes of palladium(II) ($RCO_2PdOO.Bu^t)_4$ have been synthesised. They are highly effective reagents for the selective stoichiometric oxidation of terminal olefins at the usual temperatures.[165] In the presence of an excess of *tert*-butyl peroxide, the oxidation reaction is catalytic.

$$Bu^tOOH + R'CH{=}CH_2 \xrightarrow{Pd(OCOR)_2} \longrightarrow Bu^tOH + R'{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

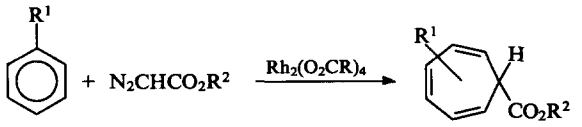
It was found that the rate of formation (indicated in brackets below) of, for example, 2-hexanone increases by two orders of magnitude on passing from the acetate to the trifluoroacetate in the following series of R: CF_3 (130), C_5H_{11} (80), CCl_3 (60), CH_3 (1).

The interaction of palladium complexes such as $Pd(OAc)_2$, $Pd(OPr)_2$, $Pd(O_2CCF_3)_2$, and $Pd(PPh_3)_4$ with H_2O_2 or K_2O_4 leads to the formation of superoxo-complexes of two types differing in the mode of coordination of the molecular oxygen radical-anion to the metal (η^1- or η^2-type of coordination) and hence in the reactivity with respect to olefins and carbon monoxide.[166]

Dirhodium(II) tetracarboxylate exhibits a catalytic activity in olefin oxidation reactions and in the conversion of the latter into cyclopropane derivatives.[167] The presence of the trifluoroacetate group ensures a high selectivity in the formation of epoxycyclohexanol in the oxidation of cyclohexene.



The addition of a carbenoid species to an aromatic compound is controlled by electronic factors. The effectiveness of the catalyst depends greatly on the electron-accepting capacity of the carboxylate ligand.[168]

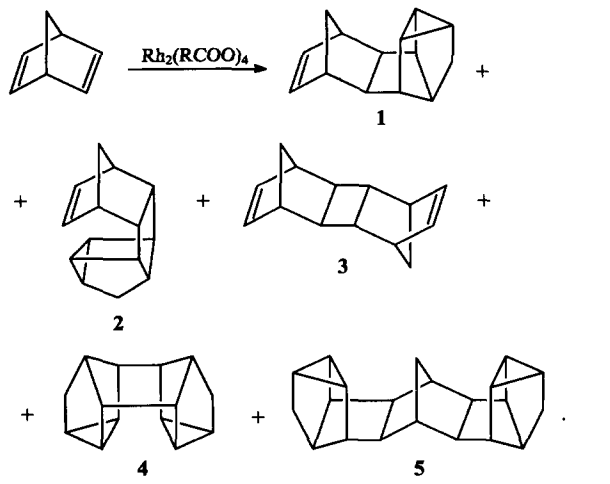


For example, the data for benzene are as follows:

Acid	pK_a	Yield (%)
CF_3COOH	0.23	100
C_6H_5COOH	1.48	89
CH_3OCH_2COOH	3.57	30
CH_3COOH	4.76	7
HCOOH	5.03	5

Dirhodium(II) tetracarboxylates $Rh_2(CO_2R)_4$ (R = CH_3, CCl_3, CF_3) have been investigated as catalysts for the cyclodimerisation of norbornadiene. It was found that in their presence the reaction proceeds with the preferential formation of *exo,endo*- and *endo,endo*-hexacyclo[9.2.1.$0^{2,10}$.$0^{3,7}$.$0^{4,9}$.$0^{6,8}$]-tetradec-12-enes (compounds **1** and **2**), but, depending on the reaction conditions, the pentacyclic dimers **3**, binor S **4**, and the norbornadiene trimer *endo,exo,endo*-decacyclo-[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,19}$.$0^{14,16}$.$0^{15,19}$]heneicosane **5** may be formed (Scheme 2).[30] The catalytic activity of the complexes increases with enhancement of the electron-accepting properties of the ligand in the sequence $Rh_2(O_2CCH_3)_4$ < $Rh_2(O_2CCCl_3)_4$ < $Rh_2(O_2CCF_3)_4$.

Scheme 2



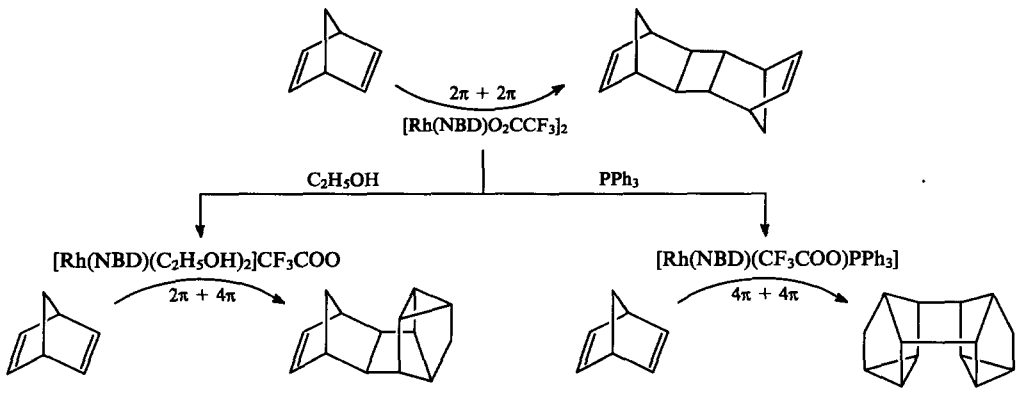
The cyclodimerisation reaction was investigated in detail in the presence of $Rh_2(O_2CCF_3)_4$. It was shown that di(μ-trifluoroacetato)bis(norbornadiene)dirhodium(I), formed on reduction of $Rh_2(O_2CCF_3)_4$ by norbornadiene, is catalytically active.[169] A similar reaction was not observed for other olefins and dienes. The interaction of $Rh_2(O_2CCF_3)_4$ with olefins and dienes[170,171] also leads, like the interaction with norbornene,[172] to the rapid and reversible formation of axial monoadducts, the structure of one of which has been investigated.[173]

The interaction of rhodium(II) with norbornadiene (NBD) has been investigated spectrophotometrically and it has been shown that the reduction of $Rh_2(O_2CCF_3)_4$ proceeds via the intermediate formation of rhodium complexes of norbornadiene of the type $Rh_2(O_2CCF_3)_4$.NBD differing in the coordination of norbornadiene.[169] For the ratio $Rh_2(O_2CCF_3)_4$: NBD = 1 : 1, an adduct is formed in which the Rh—Rh bond is retained, which was demonstrated by the formation of the familiar complex $Rh_2(O_2CCF_3)_4.2PPh_3$ via the reaction of the adduct with PPh_3. On treatment with an excess of norbornadiene or polar agents such as alcohol and acetone, rhodium(II) is reduced in the adduct to rhodium(I) with formation of $[Rh(O_2CCF_3)NBD]_2$. The observed rate constants for the reduction of $Rh_2(O_2CCF_3)_4$ and $Rh_2(O_2CCH_3)_4$ by norbornadiene, measured at 90 °C, amounted to 9.26×10^{-3} and 0.31×10^{-3} litre $mol^{-1}s^{-1}$ respectively, which agrees with the results of the electrochemical reduction of rhodium(II) carboxylates.[174] The selectivity in the formation of cyclic norbornadiene dimers in the presence of $[Rh(O_2CCF_3)NBD]_2$ is determined by the ligand environment of the rhodium atom (Scheme 3).[175]

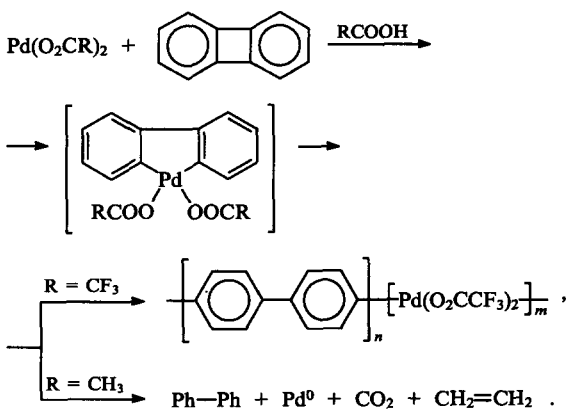
It may be that the rhodium(II) dimer disproportionates when acted upon by norbornadiene with formation of the intermediate $(NBD)Rh^I\cdots Rh^{III}$. The reduction of rhodium(III) by norbornadiene to a rhodium(I) complex, namely $[Rh(O_2CCF_3).NBD]$, confirms this pathway in the reaction of rhodium(II) on treatment with norbornadiene.[176] Rhodium(III) trifluoroacetate interacts in alcohol with $PRPh_2$ (R = Ph, *m*-$C_6H_4SO_3Na$) to form $Rh(O_2CCF_3)(PRPh_2)_3$ and $Rh(O_2CCF_3)(CO)(PPh_3)_2$.[43]

The study of the reactions of biphenylene, a tricyclic aromatic hydrocarbon, is of interest in view of the possibility of obtaining highly conducting polymers from it.[177] It has been found that the interaction of biphenylene in solutions in carboxylic acids with palladium(II) carboxylates takes place in accordance with Scheme 4.[178]

Scheme 3



Scheme 4



This reaction pathway differs significantly from the familiar reactions of biphenylene with mercury(II) carboxylates.[179,180]

* * *

The possibility of the selective functionalisation of alkanes and aromatic compounds with participation of electrophilic metal-containing centres in trifluoroacetic acid has been demonstrated in the present review in relation to dehydrogenation, carbonylation, carboxylation, and a number of other reactions. The problem of the activation of a C—H bond in alkanes still continues to engage the attention of investigators. For example, problems of the mechanism of the electrophilic activation of hydrocarbons in solutions in protic superacids have been discussed.[181] A new effective $CBr_4 \cdot n AlBr_3$ system has been proposed for the low-temperature reactions of alkanes and cycloalkanes.[182] Alkanes and cycloalkanes have been dehydrogenated with participation of low-valence rhodium complexes.[183,184] New evidence has been presented for the intermediate formation of alkylplatinum(IV) hydride in the activation of alkanes by platinum(II) complexes.[185]

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